THERMODYNAMIC PHASE BEHAVIOR AND MISCIBILITY STUDIES OF CONFINED FLUIDS IN TIGHT FORMATIONS

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Kaiqiang Zhang, candidate for the degree of Doctor of Philosophy in Petroleum Systems Engineering, has presented a thesis titled, *Thermodynamic Phase Behavior and Miscibility Studies of Confined Fluids in Tight Formations*, in an oral examination held on May 21, 2019. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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ABSTRACT

In this study, the nanoscale-extended theoretical models and experimental nanofluidic system are developed to calculate and measure the thermodynamic phase behavior and miscibility of confined pure and mixing fluids in tight formations.

First, a new nanoscale-extended equation of state (EOS) is developed to calculate the phase behavior of confined fluids in nanopores, based on which two correlations are modified to predict the shifts of critical properties. The nanoscale-extended EOS model has been proven to accurately calculate the phase behaviour of confined fluids. The thermodynamic phase behavior of confined fluids in nanopores are substantially different from those in bulk phase. The confined critical temperature and pressure always decrease with the reducing pore radius. The shifts of critical properties are dominant factors for the phase changes of confined fluids from bulk phase to nanopores.

Second, two new nanoscale-extended alpha functions in Soave and exponential types are proposed for calculating the thermodynamic and phase properties. A novel method is proposed to determine the nanoscale acentric factors. The new alpha functions are validated for the bulk and nanoscale calculations. Moreover, the acentric factors and intermolecular attractivities are increased with the pore radius reductions at most temperatures. It should be noted that the alpha functions decrease with the pore radius reduction at the critical temperature. Furthermore, the first and second derivatives of the Soave and exponential alpha functions to the temperatures are continuous at $T \leq 4000$ K.

Third, the equilibrium two-phase compositions are analyzed to elucidate the pressure dependence of the interfacial tensions (IFTs), and the confined fluid IFTs in nanopores are calculated. The phase density difference is found to be a key factor in the parachor model
for the IFT predictions, which results in three distinct pressure ranges of the IFT vs. pressure curve. The IFTs in bulk phase of the hydrocarbon systems are always higher than those in nanopores. The feed gas to liquid ratio (FGLR), temperature, pore radius, and wall-effect distance are found to have different effects on the IFTs in bulk phase and nanopores.

Fourth, a new interfacial thickness-based diminishing interface method (DIM) and a nanoscale-extended correlation are developed to determine the minimum miscibility pressures (MMPs) in bulk phase and nanopores. Using DIM, the MMP is determined by extrapolating \((\partial \delta / \partial P)_T\) to zero. Physically, the interface between fluids diminishes and the two-phase compositional change completes at the determined MMP from the DIM. The developed correlation is proposed as a function of the reservoir temperature, molecular weight of \(C_{5+}\), mole fraction ratios of volatile to intermediate components in oil and gas samples, and pore radius. The new correlation provides the accurate MMPs with overall percentage average absolute deviations (AADs%) of 5.21% in bulk phase and 6.91% in nanopores.

Fifth, thermodynamic miscibility of confined fluids in nanopores are studied. The thermodynamic free energy of mixing and solubility parameter are quantitatively determined to evaluate the fluid miscibility in nanopores. The liquid–gas miscibility is beneficial from the pore radius reduction and the intermediate hydrocarbons perform better with the liquid \(C_8\) in comparison with the lean gas (e.g., \(N_2\) and \(CH_4\)). Moreover, the molecular diameter of single liquid molecule is determined to be the bottom limit, the pore radius above which is concluded as a necessary condition for the liquid–gas miscibility.

Last, a series of nanofluidic experiments were conducted to measure the static phase behavior of confined fluids and verify the calculated data from some theoretical models.
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DEDICATIONS

To Lirong

Life is Perfect with You
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NOMENCLATURE

Notations

$a$ equation of state constant
$a_i$ empirical coefficient
$A$ surface area
$A_r$ reduced surface area
$b$ equation of state constant
$c$ coefficients
$C_p$ constant-pressure heat capacity
$C_V$ constant-volume heat capacity
$d$ empirical coefficient
$d_p$ pore diameter
$E$ overall energy state
$E^{conf}$ configurational energy
$f$ empirical coefficient
$F$ Helmholtz free energy
$F_{pr}$ fraction of the confined molecules
$g$ empirical coefficient
$G$ free energy of mixing
$h$ Planck’s constant
$H$ enthalpy of mixing
$i$ empirical coefficient
$j$ empirical coefficient
\( k \)  
Boltzmann constant

\( L \)  
length

\( m \)  
molecular mass

\( m_E \)  
\( m \) function in exponential type

\( m_{E,NP} \)  
nanoscale-extended \( m \) function in exponential type

\( m_S \)  
\( m \) function in Soave type

\( m_{S,NP} \)  
nanoscale-extended \( m \) function in Soave type

\( n \)  
moles

\( N \)  
number of molecules

\( N_A \)  
Avogadro constant

\( P \)  
system pressure

\( P_c \)  
critical pressure in bulk phase

\( P_{\text{cap}} \)  
capillary pressure

\( P_{\text{cp}} \)  
critical pressure in nanopores

\( p_i \)  
parachor of \( i^{th} \) component

\( P_L \)  
pressure of the liquid phase

\( P_V \)  
pressure of the vapour phase

\( P_{r,NP} \)  
reduced pressure in nanopores

\( q_{\text{int}} \)  
internal partition function

\( Q \)  
canonical partition function

\( R \)  
universal gas constant

\( R^2 \)  
correlation coefficient

\( r_p \)  
pore radius
\( S \)  
entropy of mixing

\( T \)  
system temperature

\( T_c \)  
critical temperature in bulk phase

\( T_{cp} \)  
critical temperature in nanopores

\( T_r \)  
reduced temperature

\( T_{r,NP} \)  
reduced temperature in nanopores

\( U \)  
potential energy

\( U_0 \)  
internal energy of the ideal gas

\( V \)  
system volume

\( V_g \)  
gas phase volume

\( V_l \)  
liquid phase volume

\( V_r \)  
reduced volume

\( x_i \)  
mole percentage of \( i^{th} \) component in the liquid phase

\( y_i \)  
mole percentage of \( i^{th} \) component in the vapour phase

\( Z \)  
configuration partition function

**Greek letters**

\( \alpha \)  
alpha function

\( \alpha_{T-E} \)  
exponential-type alpha function

\( \alpha_{T-S} \)  
Soave-type alpha function

\( \alpha_{T-E,NP} \)  
nanoscale-extended exponential-type alpha function

\( \alpha_{T-S,NP} \)  
nanoscale-extended Soave-type alpha function

\( \beta \)  
excluded volume per fluid molecule
$\Lambda$ de Broglie wavelength

$\gamma$ interfacial tension

$\varepsilon_{\text{LJ}}$ Lennard–Jones energy parameter

$\varepsilon_{\text{sw}}$ square-well energy parameter

$\sigma_{\text{LJ}}$ Lennard–Jones size parameter

$\rho_{\text{max}}$ molecular density of the close-packed fluid

$\rho_\ell$ density of the liquid phase

$\rho_v$ density of the vapour phase

$\delta$ Hildebrand solubility parameter

$\theta$ geometric term

$\phi$ solvent concentration

$\pi$ internal pressure

$\chi_{\text{CO}_2}$ CO$_2$ solubility in the original dead crude oil

$\omega$ Pitzer acentric factor

$\omega_{\text{NP}}$ nanoscale-extended acentric factor

**Subscripts**

asp Asphaltenes

brine Brine

c Critical

cell IFT cell

CH$_4$ Methane

C$_2$H$_6$ Ethane
C₃H₈  Propane
C₈H₁₈  Octane
C₁₀H₂₂  Decane
C₁₈H₃₈  Octadecane
CO₂  Carbon dioxide
eq  Equilibrium
gas  Gas
HC  Hydrocarbon
in  Initial
inj  Injection
lab  Laboratory
m  Mass
max  Maximum
N₂  Nitrogen
oi  Initial oil
oil  Oil
res  Reservoir
sat  Saturation
w  Water
wc  Connate water

*Acronyms*

AAD  average absolute deviation
ADSA  axisymmetric drop shape analysis
API   American petroleum institute
CMG  computer modelling group
DIM  diminishing interface method
EOS  equation of state
EOR  enhanced oil recovery
exp  alpha function in exponential type
FGSR Faculty of Graduate Studies & Research
HC  hydrocarbon
IEA  International Energy Agency
IFT  interfacial tension
LJ  Lennard–Jones
MAD maximum absolute deviation
MCM multi-contact miscibility
M-exp nanoscale-extended alpha function in exponential type
m–m molecule–molecule
MMP minimum miscibility pressure
M-Soave nanoscale-extended alpha function in Soave type
m–w molecule–wall
MW  molecular weight
OOIP original oil-in-place
PR  Peng–Robinson
PTRC Petroleum Technology Research Centre
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>P–V</td>
<td>pressure–volume</td>
</tr>
<tr>
<td>PVT</td>
<td>pressure–volume–temperature</td>
</tr>
<tr>
<td>RBA</td>
<td>rising-bubble apparatus</td>
</tr>
<tr>
<td>RK</td>
<td>Redlich–Kwong</td>
</tr>
<tr>
<td>SRK</td>
<td>Soave–Redlich–Kwong</td>
</tr>
<tr>
<td>sw</td>
<td>square–well</td>
</tr>
<tr>
<td>vdB</td>
<td>van der Waals</td>
</tr>
<tr>
<td>VIT</td>
<td>vanishing interfacial tension</td>
</tr>
<tr>
<td>VLE</td>
<td>vapour–liquid equilibrium</td>
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CHAPTER 1  INTRODUCTION

1.1 TIGHT OIL AND GAS RESERVOIRS

Hydrocarbon reservoirs can be categorized into three triangle classifications in Figure 1.1, where the abundance, quality, and required technology for the hydrocarbon recovery are demonstrated through their specific positions (Aguilera, 2014; Martin et al., 2010). The concept of the resource triangle was initially proposed by Masters (1979), which was expressed to be distributed lognormally in nature, as some other natural resources, by Holditch (2006) (Holditch, 2006; Masters, 1979). As shown in Figure 1.1, the highest-level resources, which refer to the conventional hydrocarbon reservoirs, are easily explored and produced but in a small amount. Lower-level resources, that is the unconventional hydrocarbon reservoirs, have an abundant original amount in place (OAIP) but are much more difficult to be developed. More specifically, typical unconventional reservoirs include the tight and shale oil/gas reservoirs, heavy oil reservoirs, coalbed methane reservoirs, and gas hydrate (Shahamat, 2014), all of which are of critical importance to the future energy supply for the society. Recently, the tight and shale oil and gas reservoirs draw special attentions of the petroleum industry because of their huge OAIP and complex recovery technologies, such as the reservoir stimulations and enhanced oil recovery (EOR) (L. Jin et al., 2017; Weng et al., 2011).

The terminologies of “tight oil” and “shale oil” were not distinguished clearly and usually interchangeably used in the previous publications (Kuuskraa et al., 2013; Ozkan et al., 2011). In general, tight oil formations refer to all the formations containing oil with a low to ultralow permeability, which include the sandstone, carbonate, and shale formations.
Figure 1.1 Pyramid of the world oil and gas resources (Aguilera, 2014).
(Yu et al., 2015). It is clear that the shale oil formation is a sub-category of the tight oil formations. Although the Tight Oil (Formation/Production) is commonly preferred in the formal usages as a result of its broader definition (Kuuskraa et al., 2013), the term of tight oil will be used in this study in order to correctly express the target reservoirs. It should be noted that another two terminologies of “shale oil” and “oil shale” cannot be interchangeably used as aforementioned. Therein, oil shale is sort of a precursor of crude oil (i.e., a teenage oil) that constitutes the fundamental components of conventional oils (Maugeri, 2013). More precisely, the distinguishing characteristics of the oil shale is its special organic carbon that it has not been transformed into crude oil (Dyni, 2003). In this case, the oil shale formations have low porosity and permeability, which is termed as a source rock with a Type I kerogen (Lewan and Roy, 2011). Normally, shale oil formations with depths of at least 15,000 feet are deeper than oil shales (Maugeri, 2013). On the other hand, the “tight gas reservoir” and “shale gas reservoir” can be distinguished, the former of which is defined that the formation permeability is equal to or less than 0.1 md (100 micro-Darcy) and the latter of which is defined as a lithostratigraphic unit with less than 50% organic matter in weight, less than 10% grain size of the sedimentary clasts greater than 62.5 micrometers, and more than 10% grain size of the sedimentary clasts smaller than 4 micrometers (Euzen, 2011; Spencer, 1989; Spencer et al., 2010). Various definitions in terms of the tight and shale gas reservoirs have been stated in the previous literature. The most distinguishable feature of the shale gas reservoir is that the grains and pores in shale are smaller than those in tight formations, even though the grains and pores in tight formations are much smaller than the conventional formations (Clarkson et al., 2016). Accordingly, the gas storage in the tight and shale formations can be much more
complicated in comparison with the conventional gas reservoirs, which was roughly
described as follows: 1. Gas adsorbed into the kerogen materials; 2. Free gas trapped in
nonorganic interparticle (matrix) pores; 3. Free gas trapped in microfracture pores; 4. Free
gas stored in hydraulic fractures created during the stimulation of shale reservoirs; 5. Free
gas trapped in a pore network developed within the organic matter or kerogen (Aguilera,
2014).

1.2 Purpose and Scope of This Study

The purpose of this study is to systematically investigate the complex phase behavior
and miscibility of confined fluids in nanopores of the tight and shale reservoirs, including
the developments and modifications of a series equations of state (EOSs), thermodynamic
models, theoretical calculations, and analytical/semi-analytical correlations. The specific
research objectives and the overall scope of this study are listed as follows:

1. To develop a nanoscale-extended EOS by considering the confinement effects
   and intermolecular interactions and evaluate the fluid phase behavior in
   nanopores;

2. To modify the existing alpha functions to the nanometer scale and evaluate the
   alpha function and its derivatives as well as their effects on the phase behavior
   in bulk phase and nanopores;

3. To calculate the interfacial tensions (IFTs) of confined fluids through modified
   EOSs and evaluate the pressure-dependence IFTs at different conditions in bulk
   phase and nanopores;
4. To determine the minimum miscibility pressures (MMPs) through a new theoretical model, i.e., the diminishing interface method (DIM), and a nanoscale-extended empirical correlation;

5. To thermodynamically quantify the miscibility and specifically analyze the miscibility developments;

6. To experimentally measure the static phase behavior of confined fluids in nanopores and verify some corresponding theoretical models aforementioned.

1.3 Outline of the Dissertation

This thesis consists of eight chapters. Specifically, Chapter 1 gives an introduction to the thesis topic along with the purpose and the scope of this study. Chapter 2 presents the development and application of a nanoscale-extended EOS by including the effects of pore radius and intermolecular interactions. The phase behavior of confined fluids is specifically investigated by means of the developed EOS. In Chapter 3, two existing empirical alpha functions are extended to the nanometer scale. The modified empirical alpha functions are applied to calculate the phase and thermodynamic properties in bulk phase and nanopores. Chapter 4 describes the developments of modified EOSs to calculate the IFTs in bulk phase and nanopores. The pressure-dependence of bulk and confined IFTs at different temperatures, feed compositions, and pore radii are also evaluated. In Chapter 5, a new DIM technique and a nanoscale-extended empirical correlation are proposed to calculate the MMPs in bulk phase and nanopores. On the basis of a series calculated MMPs for pure and mixing fluids, the effects of temperature, fluid compositions, and pore radius on the MMPs in bulk phase and nanopores are specifically evaluated. In Chapter 6, the miscible state is thermodynamically described and quantified through the thermodynamic free
energy of mixing and solubility parameter coupled with the developed nanoscale-extended EOS. In Chapter 7, a nanofluidic system is developed and applied to measure the static phase behavior of confined fluids in nanopores and verify the calculated data from some proposed theoretical models. Chapter 8 summarizes major scientific findings of this study and four technical recommendations are stated for future studies.
CHAPTER 2  NANOSCALE-EXTENDED EQUATION OF STATE

2.1  Introduction

In recent years, confined fluids in porous media attract more and more attentions due to its wide applications, for example, inorganic ions pass through the cell membranes (Cooper and Hausman, 2004), industrial separation process (Ganapathy et al., 2015) and heterogeneous catalysis (Tanimu et al., 2017), and oil/gas production from shale reservoir (Ambrose et al., 2012). The confinement effect becomes much strengthened when the pore radius reduces to the nanometric scale, which is comparable to a molecular size and causes dramatic changes of fluid phase properties even in qualitative views (Dong et al., 2016). In a confined fluid, for instance, the slight energy dissipations caused by frictions can induce a series of significant static or dynamic changes (e.g., shear stress, compressibility, or viscosity), which may not even be detected in bulk phase (Meng et al., 2015). In general, the phase behaviour of the confined fluids in nanopores are studied mainly from the theoretical prospective while few laboratory experiments are available for confined fluids in nanopores because of the extremely high requirements of precision, enlargement in observation/imaging system, and associated cost (Lifton, 2016). The theoretical methods, which include equation of state (EOS) (Teklu et al., 2014b; Zhang et al., 2017b), Kelvin equation (Digilov, 2000; Melrose, 1989), density functional theory (Fan et al., 2009; Rossi et al., 2015), and molecular simulation (Grzelak et al., 2010; Uddin et al., 2016), are extensively used to study the phase behaviour of the confined fluids in nanopores. However, the last three theoretical methods are time-consuming due to their intensive mathematical and computational frameworks, plus some underlying physical mechanisms cannot be clearly revealed. Hence, the cubic EOS is always regarded as an available and appropriate
approach to calculate the phase properties of the confined fluids in nanopores due to its simplicity and accuracy in calculation.

Nowadays, unconventional oil reservoirs draw remarkable attentions because of their tremendous amount of original oil in place (OOIP) and continuously increasing demands from the human society (Giles, 2004). The shale oil/gas in the extremely tight formation, as a typical example of confined fluids in nanopores, undergo substantial phase behaviour changes, such as the shifts of critical properties, saturation pressures and density variations, due to the shifts of the critical properties (Bao et al., 2017a; Molla and Mostowfi, 2017). For example, the bubble point pressure of a Bakken oil–CO$_2$ system is found to be significantly decreased while the upper dew-point pressure increases and lower dew-point pressure decreases with an increasing confinement effect (Teklu et al., 2014b). The above-mentioned fluid phase behaviour studies in nanopores are all based on two existing correlations for predicting the shifts of critical temperature and pressure under a strong confinement effect (Zarragoicoechea and Kuz, 2004). Although the correlations have been proven to be accurate to certain extent, a further modification is still necessary for complex mixing fluids like shale oil, gas etc.

In this chapter, a semi-analytical EOS is developed to calculate the thermodynamic phase behaviour of confined pure and mixing fluids in nanopores, on a basis of which two correlations are modified to predict the shifts of critical properties under the confinement effect. Moreover, an improved EOS model with the modified correlations is proposed to calculate the phase properties of three mixing fluids, which are compared with and validated by the literature results.
2.2 Materials

Pure CO₂, N₂, and a series of alkanes from C₁–C₁₀ are used, whose critical properties (i.e., temperature, pressure, and volume), van der Waals EOS constants, and Lennard-Jones potential parameters are summarized (Mansoori and Ali, 1974; Whitson and Brule, 2000; Yu and Gao, 2000) and listed in Table 2.1. In addition, as three hydrocarbon mixture systems, a ternary mixture of 4.53 mol.% \( n\text{-}C_4H_{10} \) + 15.47 mol.% \( i\text{-}C_4H_{10} \) + 80.00 mol.% \( C_8H_{18} \) (Wang et al., 2014) and a live light crude oil (i.e., oil B) (Teklu et al., 2014b) are applied to study the phase behaviour of the mixture fluids. The compositional analyses of the ternary HC mixture and live oil systems as well as the detailed experimental set-up and procedures for preparing the oil samples were specifically introduced in the literature (Zhang and Gu, 2016a, 2016b, 2015).

2.3 Methods

2.3.1 Critical properties of confined fluid

In this chapter, the conventional van der Waals EOS (vdW-EOS) is modified to describe the confined fluids in nanopores (Zhang et al., 2018a). Although there are many existing EOS, the vdW-EOS is still the simplest cubic EOS to be capable of accurately predicting the vapour–liquid equilibrium (VLE), critical properties, and fluid stability/metastability (Stanley, 1971). Suppose that a nanoscale pore system, as shown in Figure 2.1, consists of some confined particles via any potential. Here, pressure \( \vec{P}(P_i = x, r) \) is expressed as a diagonal tensor due to the confinement-induced asymmetry, plus the fluid molecules are not perfectly elastic (Zarragoicoechea and Kuz, 2002). Hence, the Gibbs free energy \( (G) \) is given by (Gibbs, 1961),
Table 2.1

Recorded critical properties (i.e., temperature, pressure, and volume), van der Waals equation of state (EOS) constants, and Lennard-Jones potential parameters of CO$_2$, N$_2$, and C$_1$–C$_{10}$ (Mansoori and Ali, 1974; Whitson and Brule, 2000; Yu and Gao, 2000).

<table>
<thead>
<tr>
<th>Component</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (Pa)</th>
<th>$V_c$ (m$^3$/mol)</th>
<th>$a$ (Paxm$^6$/mol$^2$)</th>
<th>$b$ (m$^3$/mol)</th>
<th>$\varepsilon/k$ (K)</th>
<th>$\sigma$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>304.2</td>
<td>7.38×10$^6$</td>
<td>9.40×10$^{-5}$</td>
<td>1.02×10$^{-48}$</td>
<td>7.12×10$^{-29}$</td>
<td>294</td>
<td>2.95×10$^{-10}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>126.2</td>
<td>3.39×10$^6$</td>
<td>8.95×10$^{-5}$</td>
<td>3.78×10$^{-49}$</td>
<td>6.43×10$^{-29}$</td>
<td>364</td>
<td>3.32×10$^{-10}$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>190.6</td>
<td>4.60×10$^6$</td>
<td>9.90×10$^{-5}$</td>
<td>6.34×10$^{-49}$</td>
<td>7.14×10$^{-29}$</td>
<td>207</td>
<td>3.57×10$^{-10}$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>305.4</td>
<td>4.88×10$^6$</td>
<td>1.48×10$^{-4}$</td>
<td>1.54×10$^{-48}$</td>
<td>1.08×10$^{-28}$</td>
<td>155</td>
<td>3.61×10$^{-10}$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>369.8</td>
<td>4.25×10$^6$</td>
<td>2.03×10$^{-4}$</td>
<td>2.33×10$^{-48}$</td>
<td>1.59×10$^{-28}$</td>
<td>120</td>
<td>3.43×10$^{-10}$</td>
</tr>
<tr>
<td>$i$-C$<em>4$H$</em>{10}$</td>
<td>408.1</td>
<td>3.65×10$^6$</td>
<td>2.63×10$^{-4}$</td>
<td>3.42×10$^{-48}$</td>
<td>1.37×10$^{-28}$</td>
<td>140</td>
<td>3.85×10$^{-10}$</td>
</tr>
<tr>
<td>$n$-C$<em>4$H$</em>{10}$</td>
<td>425.2</td>
<td>3.80×10$^6$</td>
<td>2.55×10$^{-4}$</td>
<td>3.84×10$^{-48}$</td>
<td>1.94×10$^{-28}$</td>
<td>118</td>
<td>3.91×10$^{-10}$</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$</td>
<td>469.6</td>
<td>3.37×10$^6$</td>
<td>3.04×10$^{-4}$</td>
<td>5.27×10$^{-48}$</td>
<td>2.41×10$^{-28}$</td>
<td>145</td>
<td>3.96×10$^{-10}$</td>
</tr>
<tr>
<td>C$<em>6$H$</em>{14}$</td>
<td>507.5</td>
<td>3.29×10$^6$</td>
<td>3.44×10$^{-4}$</td>
<td>6.89×10$^{-48}$</td>
<td>2.91×10$^{-28}$</td>
<td>199</td>
<td>4.52×10$^{-10}$</td>
</tr>
<tr>
<td>C$<em>7$H$</em>{16}$</td>
<td>543.2</td>
<td>3.14×10$^6$</td>
<td>3.81×10$^{-4}$</td>
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<td>3.38×10$^{-28}$</td>
<td>206</td>
<td>4.70×10$^{-10}$</td>
</tr>
<tr>
<td>C$<em>8$H$</em>{18}$</td>
<td>570.5</td>
<td>2.95×10$^6$</td>
<td>4.21×10$^{-4}$</td>
<td>1.04×10$^{-47}$</td>
<td>3.82×10$^{-28}$</td>
<td>213</td>
<td>4.89×10$^{-10}$</td>
</tr>
<tr>
<td>C$<em>9$H$</em>{20}$</td>
<td>598.5</td>
<td>2.73×10$^6$</td>
<td>4.71×10$^{-4}$</td>
<td>1.24×10$^{-47}$</td>
<td>4.49×10$^{-28}$</td>
<td>220</td>
<td>5.07×10$^{-10}$</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{22}$</td>
<td>622.1</td>
<td>2.53×10$^6$</td>
<td>5.21×10$^{-4}$</td>
<td>1.46×10$^{-47}$</td>
<td>5.07×10$^{-28}$</td>
<td>226</td>
<td>5.23×10$^{-10}$</td>
</tr>
</tbody>
</table>
Figure 2.1 Schematic diagram of (a) micro- and nano-pore network model for shale matrix (Zhang et al., 2015) and (b) the nanoscale pore system in this study.
\[ G(p,T) = U + PV - TS \quad (2.1) \]

where \( U \) is the internal energy, \( P \) is the pressure, \( V \) is the system volume, \( T \) is the temperature, and \( S \) is the entropy. Therein, Legendre transforms of the internal energy gives (Islam et al., 2015),

\[ dU = TdS - PdV \quad (2.2) \]

\[ P_x = -\left. \frac{\sigma^2}{A} \frac{\partial F}{\partial L_x} \right|_{r,L_x}, \quad P_r = -\left. \frac{\sigma^2}{L_x} \frac{\partial F}{\partial A} \right|_{r,A} \]

where \( \sigma \) is the Lennard-Jones size parameter, \( A \) is the contact surface area, \( A = \pi \left( \frac{r_p}{\sigma} \right)^2 \), \( r_p \) is the pore radius, \( L_x \) is the length in axial direction, and \( F \) is the Helmholtz free energy.

From the previous study (Zarragoicoechea and Kuz, 2002), the Helmholtz free energy for a confined system consisting \( n \) particles interacting through the Lennard-Jones potential \( U(r_{12}) \) is presented,

\[ F = F_0 - \frac{kT N^2}{2V^2} \int \int (e^{-U(r_{12})/kT} - 1)dV_1dV_2 \quad (2.3) \]

\[ U(r_{12}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{12}} \right)^{12} - \left( \frac{\sigma}{r_{12}} \right)^6 \right] \]

where \( F_0 \) is the Helmholtz free energy of ideal gas, \( k \) is the Boltzmann constant, and \( \epsilon \) is the Lennard-Jones energy parameter. Given that the vdW-EOS is used in this study, whose standard form is \( P = \frac{RT}{V-b} - \frac{a}{V^2} \), \( R \) is the universal gas constant, \( a \) and \( b \) are the EOS constants. By following the derivations from the literature (Islam et al., 2015) and the assumption of \( r_{12} > \sigma \), the analytical solution of Eq. (2.3) is shown,
\[ F = F_0 + \frac{kTN^2}{V} b + \frac{kTN^2}{2V^2} \int_{r_1 > \sigma} \frac{U(r_2)}{kT} dV_1 dV_2 \]  

(2.4)

Then, the integral part of Eq. (2.4) is solved semi-analytically as,

\[ \frac{1}{V} \int_{r_1 > \sigma} \frac{U(r_2)}{kT} dV_1 dV_2 = \frac{4\varepsilon}{kT} \sigma^3 f(A) \]  

(2.5)

\[ f(A) = c_0 + \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \]

where \( c_0 = -\frac{8\pi}{9} \), \( c_1 = 3.5622 \), and \( c_2 = -0.6649 \). It should be noted that the value of \( c_0 \) was calculated by solving Eq. (2.5) analytically, while the values of \( c_1 \) and \( c_2 \) are obtained from a non-linear least-square method (Katjamaa and Orešič, 2005). Figure 2.2 shows the calculated \( f(A) \) values from Eq. (2.5) and fitting curve by tuning \( c_1 \) and \( c_2 \). It is obvious that the fitting curve matches well with the calculated values. On a basis of Eqs. (2.4) and (2.5),

\[ P_x = \frac{NkT}{V - Nb} - \frac{N^2}{V^2} [a - \varepsilon \sigma^3 (3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A})] \]  

(2.6a)

\[ P_t = \frac{NkT}{V - Nb} - \frac{N^2}{V^2} [a - 2\varepsilon \sigma^3 (\frac{c_1}{\sqrt{A}} + \frac{c_2}{A})] \]  

(2.6b)

The critical temperature, pressure, and volume can be solved at the condition of

\[ \left. \frac{\partial P_r}{\partial V} \right|_r - \left. \frac{\partial^2 P_t}{\partial V^2} \right|_r = 0 \]  

(Whitson and Brule, 2000), which are shown as follows,

\[ T_{cp} = \frac{8\varepsilon \sigma^3}{27kb} \left[ a - 2\varepsilon \sigma^3 (\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}) \right] \]  

(2.7a)
Figure 2.2 Calculated and correlated values of the integral part from Eq. (2.5).
\[ P_{cp} = \frac{a - 2\epsilon \sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)}{27b^2} \]  \hspace{1cm} (2.7b)

\[ V_{cp} = 3bN \]  \hspace{1cm} (2.7c)

In addition, Eqs. (2.6) and (2.7) can be dimensionless as,

\[ \bar{P}_x = \frac{\bar{T}}{\bar{V} - \bar{b}} - \frac{\bar{a} - (3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A})}{\bar{V}^2} \]  \hspace{1cm} (2.8a)

\[ \bar{P}_i = \frac{\bar{T}}{\bar{V} - \bar{b}} - \frac{\bar{a} - 2\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}}{\bar{V}^2} \]  \hspace{1cm} (2.8b)

and,

\[ \bar{T}_{cp} = \frac{8}{27b} [\bar{a} - 2\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}] \]  \hspace{1cm} (2.9a)

\[ \bar{P}_{cp} = \frac{\bar{a} - 2\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}}{27\bar{b}^2} \]  \hspace{1cm} (2.9b)

\[ \bar{V}_{cp} = \bar{3b} \]  \hspace{1cm} (2.9c)

where \( \bar{P} = P \sigma^3 / \epsilon \), \( \bar{T} = kT / \epsilon \), \( \bar{V} = (V / n) / \epsilon \), \( \bar{a} = a / \epsilon \sigma^3 \), and \( \bar{b} = b / \sigma^3 \). It is well known that the corresponding bulk fluid critical properties are:

\[ \bar{T}_c = \frac{8\bar{a}}{27\bar{b}}, \quad \bar{P}_c = \frac{\bar{a}}{27\bar{b}^2}, \]

\[ \bar{V}_c = 3\bar{b} \]. Hence, the shifts of critical temperature and pressure in nanopores are modified to be,

\[ \frac{\bar{T}_c - \bar{T}_{cp}}{\bar{T}_c} = 2\frac{c_1}{\sqrt{\pi a r_p}} \frac{\sigma}{r_p} + 2\frac{c_2}{\pi a r_p} \left( \frac{\sigma}{r_p} \right)^2 = 0.7197 \frac{\sigma}{r_p} - 0.0758 \left( \frac{\sigma}{r_p} \right)^2 \]  \hspace{1cm} (2.10a)
The shifts of critical temperature and pressure of a mixture can be calculated by applying a simple mixing rule (Whitson and Brule, 2000),

\[ \frac{P_c - P_{cp}}{P_c} = 2 \frac{C_1}{\sqrt{\pi a}} \frac{\sigma}{r_p} + 2 \frac{C_2}{\pi a} \left( \frac{\sigma}{r_p} \right)^2 = 0.7197 \frac{\sigma}{r_p} - 0.0758 \left( \frac{\sigma}{r_p} \right)^2 \]  

(2.10b)

The shifts of critical temperature and pressure of a mixture can be calculated by applying a simple mixing rule (Whitson and Brule, 2000),

\[ T_c = \sum x_i T_{c_i}, \quad P_c = \sum x_i P_{c_i} \]  

(2.11)

### 2.3.2 Vapour–liquid equilibrium

The modified vdW-EOS is proposed to calculate the VLE properties in nanopores. The shifts of critical properties (i.e., critical temperature and pressure) of the confined fluids are predicted by using the modified equations from Eqs. (2.10a) and (2.10b) in this study. In addition, the liquid and vapour phases are assumed to be the wetting phase and non-wetting phase, respectively (Nojabaei et al., 2013). Thus the capillary pressure \( P_{cap} \) is,

\[ P_{cap} = P_v - P_L \]  

(2.12)

where \( P_v \) is the pressure of the vapour phase and \( P_L \) is the pressure of the liquid phase. On the other hand, the capillary pressure can be expressed by Young–Laplace equation,

\[ P_{cap} = \frac{2\gamma}{r_p} \cos \theta \]  

(2.13)

where \( \gamma \) is the interfacial tension and \( \theta \) is the contact angle of the vapour–liquid interface with respect to the pore surface, which is assumed to be 30° according to the experimental results in the literature (Wang et al., 2014). Therein, the IFT is estimated by means of the Macleod–Sugden equation (Sugden, 1924),

\[ \gamma = (\rho_L \sum_{i=1}^{r} x_i p_i - \rho_V \sum_{i=1}^{r} y_i p_i) \]  

(2.14)

where \( x_i \) and \( y_i \) are the respective mole percentages of the \( i^{th} \) component in the liquid and
vapour bulk phases, \( i = 1, 2, \ldots, r \); \( r \) is the component number in the mixture; and \( \rho_i \) is the parachor of the \( i^\text{th} \) component.

The VLE calculations based on the modified vdW-EOS require a series of iterative computations through, for example, the Newton–Raphson method. Figure 2.3 shows the flowchart of the VLE calculation process, by means of which the logic and correctness of each step have been positively checked and verified. The predicted pressure–volume–temperature (PVT) data for the \( i\text{C}_4–n\text{C}_4–\text{C}_8 \) system are summarized and compared with the measured data in Table 2.2. The computational time of the proposed model, in this study, is fast for the pure component case or slightly more for the mixing fluid case calculations on a personal computer. Overall, the modified vdW-EOS in this study is validated to be accurate and efficient in terms of the phase behaviour of the hydrocarbon mixture systems calculations, whose results agree well with the measured data. However, it is necessary to point out that the applications of the Lennard–Jones potential, vdW-EOS, and some empirical quantities may cause some limitations for the proposed model. For example, the proposed model may be inaccuracy in some case calculation because the Lennard–Jones potential only has two parameters in the size and energy scales and may lose its generality for some specific components (Smit, 1992). In addition, the proposed model is developed on a basis of the vdW-EOS, which may sometimes lose its accuracy in terms of the liquid property or high temperature case calculations (Stanley, 1971).

### 2.4 Results and Discussion

The critical temperatures and pressures of \( \text{C}_2\text{H}_6 \) at the pore radii of 2–10 nm are
Figure 2.3 Flowchart of the modified van der Waals equation of state for phase properties, free energy of mixing, solubility parameter, and interfacial tension calculations at nanometric scale.
Table 2.2

Measured (Wang et al., 2014) and calculated phase properties for the \(i\text{C}_4-n\text{C}_4-C_8\) system in the microchannel of 10 µm and nanochannel of 100 nm at (a) constant pressure and (b) constant temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before flash calculation (measured)</th>
<th>After flash calculation (measured)</th>
<th>After flash calculation (this study)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>24.9</td>
<td>71.9</td>
</tr>
<tr>
<td></td>
<td>Pressure (Pa)</td>
<td>85,260</td>
<td></td>
</tr>
<tr>
<td>Liquid ((i\text{C}_4-n\text{C}_4-C_8, \text{mol.}%))</td>
<td>15.47 4.53 80.00</td>
<td>4.88 1.87 93.25</td>
<td>6.38 2.03 91.59</td>
</tr>
<tr>
<td>Vapour ((i\text{C}_4-n\text{C}_4-C_8, \text{mol.}%))</td>
<td>0 0 0</td>
<td>64.35 16.82 18.83</td>
<td>65.68 18.97 15.35</td>
</tr>
<tr>
<td>Liquid fraction (mol.%)</td>
<td>100.00</td>
<td>82.20</td>
<td>84.22</td>
</tr>
<tr>
<td>Vapour fraction (mol.%)</td>
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<td>17.80</td>
<td>15.78</td>
</tr>
<tr>
<td>IFT (mJ/m²)</td>
<td>–</td>
<td>16.24</td>
<td>17.97</td>
</tr>
<tr>
<td>(P_{\text{cap}}) in micro-channel (kPa)</td>
<td>–</td>
<td>3.38</td>
<td>2.35</td>
</tr>
<tr>
<td>(P_{\text{cap}}) in nano-channel (kPa)</td>
<td>–</td>
<td>286.91</td>
<td>199.24</td>
</tr>
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</table>

**(b) constant temperature case**

<table>
<thead>
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<th>Parameters</th>
<th>Before flash calculation (measured)</th>
<th>After flash calculation (measured)</th>
<th>After flash calculation (this study)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Pressure (Pa)</td>
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<td>426,300</td>
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<tr>
<td>Liquid ((i\text{C}_4-n\text{C}_4-C_8, \text{mol.}%))</td>
<td>61.89 18.11 20.00</td>
<td>28.59 11.15 60.26</td>
<td>21.18 8.67 70.15</td>
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<tr>
<td>Vapour ((i\text{C}_4-n\text{C}_4-C_8, \text{mol.}%))</td>
<td>0 0 0</td>
<td>75.82 21.01 3.16</td>
<td>77.89 21.14 0.97</td>
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<td>Liquid fraction (mol.%)</td>
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<td>31.78</td>
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<td>Vapour fraction (mol.%)</td>
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<td>IFT (mJ/m²)</td>
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<td>13.98</td>
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<td>(P_{\text{cap}}) in micro-channel (kPa)</td>
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<td>2.26</td>
</tr>
<tr>
<td>(P_{\text{cap}}) in nano-channel (kPa)</td>
<td>–</td>
<td>235.54</td>
<td>196.32</td>
</tr>
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</table>
calculated from Eqs. (2.7a) and (2.7b), which are compared with the calculated ones from the Grand Canonical Monte Carlo (GCMC) simulation (Pitakbunkate et al., 2016) and plotted in Figure 2.4a. The proposed model, which only consists of several simple iterations, costs less computational time in terms of the phase property calculations of the confined fluids, especially the confined mixing fluids, when compared with the GCMC simulation (Adams, 1975; Gowers et al., 2018). It is found that both the calculated critical temperatures and pressures are decreased with the reduction of the pore radius. The calculated critical temperatures from this study agree well with the GCMC values, whereas the deviations of critical pressures are relatively large. This is because only the shift of critical pressure but no capillary pressure is considered in Eqs. (2.7b). It is worthwhile to mention that the overall trends of the calculated critical pressures from the both methods are similar and the deviated values are almost same. It means the shifts of critical properties dominate the transitions of the phase properties from bulk phase to nanopores, whereas effect of the capillary pressure initially increases with the pore radius reduction but remains unchanged at certain pore level. Figure 2.4b shows the comparison of the measured shifts of critical temperatures (i.e., the solid points) for seven different components (Islam et al., 2015; Zarragoicoechea and Kuz, 2002) and calculated values (i.e., the solid line) from Eq. (2.10a). It is seen from the figure that the solid line matches the shifts of critical temperatures for various components at different pore radii, which indicates the modified correlation for predicting the shifts of critical temperature (i.e., Eq. 2.10a) is accurate and applicable for various components, particularly, the gases (e.g., CO$_2$) and alkanes. Hence, the proposed model and modified correlations have been proven to predict the phase properties and shifts of critical properties at nanometric scale in an accurate manner.
Figure 2.4a Calculated critical temperatures and pressures of C$_2$H$_6$ from the Grand Canonical Monte Carlo (GCMC) simulation (Pitakbunkate et al., 2016) and this study at the pore radius of 2–10 nm.
Figure 2.4b Measured (Islam et al., 2015; Zarragoicoechea and Kuz, 2002) and calculated shifts of the critical temperatures with the variations of the pore radii.
**Figure 2.5a** Calculated critical temperatures of CO$_2$, N$_2$, CH$_4$, C$_2$H$_6$, C$_3$H$_8$, $i$- and $n$-C$_4$H$_{10}$ and C$_8$H$_{18}$ at the pore radius of 0.4–1,000 nm.
Figure 2.5b Calculated critical pressures of CO\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, i- and n-C\textsubscript{4}H\textsubscript{10} and C\textsubscript{8}H\textsubscript{18} at the pore radius of 0.4–1,000 nm.
Figure 2.5c Calculated critical shifts of temperature or pressure of CO$_2$, N$_2$, CH$_4$, C$_2$H$_6$, and C$_8$H$_{18}$ with respect to different pore radii.
In Figures 2.5a and 2.5b, the critical temperatures and pressures of CO$_2$, N$_2$, C$_1$, C$_2$, C$_3$, i- and n-C$_4$, and C$_8$ at the pore radius of 0.4–1,000 nm are calculated, all of which are decreased with the reducing pore radius. More specifically, a slight decrease for the critical temperature/pressure initiates at $r_p = 100$ nm and lasts till $r_p = 10$ nm, after which a substantial decrease occurs with the further pore radius reduction. Moreover, the critical property of a heavier alkane is found to be higher in critical temperature and lower in critical pressure. The critical temperatures of the alkanes, especially those with high-molecular weight (MW) like C$_8$, are sensitive to the changes of pore radius when $r_p < 10$ nm. A sudden slope change occurs, for C$_8$, at $r_p = 1$ nm, after which the decrease of the critical properties becomes more slowly with the pore radius. Given that the molecular diameter of C$_8$ is 1 nm (Zhang and Gu, 2016b), thus, several C$_8$ molecules may aggregate at $r_p > 1$ nm while only one C$_8$ molecule exists at $r_p = 1$ nm. Obviously, the effect of the pore radius is stronger for some aggregated molecules (intermolecularly) rather than a single one (intramolecularly). On the other hand, CO$_2$ is a rather special case since both its critical temperature and pressure are sensitive to the pore radius. From Eqs. (2.10a) and (2.10b), the shifts of critical temperature/pressure of CO$_2$, N$_2$, C$_1$, C$_2$, and C$_8$ at different pore radii are calculated and plotted in Figure 2.5c. It is found from the figure that the linear increase of the critical temperature/pressure shifts with the reduction of pore radius is up to the limit of $\frac{\sigma}{r_p} = 0.1$, which is almost same for different components. In addition to the previous explanation that no multilayer adsorptions considered prior to the capillary condensations (Islam et al., 2015), the deviations from the linearity are also inferred to be caused by the diminishing effect of the pore radius. As the pore radius is continuously
reduced, it takes effect within a molecule (intramolecularly) rather than out of the molecule (intermolecularly). The shifts of critical properties for the heavier alkanes with respect to the pore radius are more obvious in comparison with those of the lighter components.

In Figures 2.6a–c, the calculated PVT diagrams from the original and modified EOS for CO$_2$, C$_1$, and C$_8$ at different reduced temperatures ($T_r$) and volumes ($V_r$) are presented in three and two dimensions. It is seen from Figure 2.6(a1) that the pressure is reduced with the decreasing temperature and increasing volume. A typical example at $T_r = 0.5$ is selected and plotted separately in Figure 2.6(a2) to show the differences between the pressures in bulk phase from the original EOS and in nanopores (1 nm) from the modified EOS. The figures clearly indicate that either radial or axial pressure in nanopores shifts upward (i.e., become higher) in comparison with that in bulk phase, which is attributed to the increasing confinement effect in nanopores. The PVT diagrams of C$_1$ and C$_8$ in Figures 2.6b and 2.6c share a similar overall pattern with that of CO$_2$, where the calculated pressures in nanopores are always higher than those in bulk phase from the original EOS but to different extent. It should be noted that negative pressures are present in all cases. In general, the negative pressure state for gases is considered to be physically meaningless (Whitson and Brule, 2000). This is because an approaching-zero pressure corresponds to an infinite volume from the ideal gas EOS, which obviously is not true. Meanwhile, the negative pressure state for liquids can be valid when they are stretched or under tension (Imre, 2007). The negative liquid pressure is always considered as a metastable state, which can be quantified by using the vdW-EOS. On a basis of the vdW-EOS in bulk phase and nanopores with the condition that $P = 0$,

$$RT = \frac{a(v-b)}{v^2} \quad \text{bulk phase} \quad (2.15a)$$
**Figure 2.6a1** Calculated phase diagrams of CO$_2$ bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores in 3D diagram at $T_r = 0.1−0.9$ and $V_r = 0.5−15$. 
Figure 2.6a2 Calculated phase diagrams of CO$_2$ bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores in 2D diagram at $T_r = 0.5$ and $V_r = 0.5 - 15$. 
**Figure 2.6b1** Calculated phase diagrams of CH₄ bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores in 3D diagram at $T_r = 0.1 - 0.9$ and $V_r = 0.5 - 15$. 
Figure 2.6b2 Calculated phase diagrams of CH₄ bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores in 2D diagram at $T_r = 0.5$ and $V_r = 0.5 - 15$. 
Figure 2.6c1 Calculated phase diagrams of $\text{C}_8\text{H}_{18}$ bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores in 3D diagram at $T_r = 0.1 - 0.9$ and $V_r = 0.5 - 15$. 
Figure 2.6c2 Calculated phase diagrams of C$_8$H$_{18}$ bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores in 2D diagram at $T_r = 0.5$ and $V_r = 0.5 - 15$. 
radial in nanopores \hspace{1cm} (2.15b) \\

axial in nanopores \hspace{1cm} (2.15c) \\

The right-hand side (RHS) of Eqs. 2.15(a–c) was proven to have a maximum value at \( v = 2b \) and a minimum value at \( v = b \) (Imre, 2007). Hence, the conditions of temperature and volume for the negative pressure state can be obtained as follows,

\[
0 < T < \frac{a}{4bR} \hspace{1cm} \text{bulk phase} \hspace{1cm} (2.16a)
\]

\[
0 < T < \frac{a - 2\varepsilon \sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)}{4bR} \hspace{1cm} \text{radial in nanopores} \hspace{1cm} (2.16b)
\]

\[
0 < T < \frac{a - \varepsilon \sigma^3 \left( 3 \frac{c_1}{\sqrt{A}} + 4 \frac{c_2}{A} \right)}{4bR} \hspace{1cm} \text{axial in nanopores} \hspace{1cm} (2.16c)
\]

\[
b < v < 2b \hspace{1cm} (2.17)
\]

Figure 2.7 shows the calculated bulk phase pressure as well as radial and axial pressures in nanopores of \( C_8 \) at \( V_r = 1.5 \) and \( T_r = 0.1 - 0.9 \). The pressure either in bulk phase from the original EOS or in nanopores from the modified EOS is linearly increased with the reduced temperature. Moreover, Eqs. 2.16(a–c) validate that the upper temperature limits of the negative pressure state in nanopores are lower than those in bulk phase. According to Eqs. 2.16(a–c), the upper temperature limit is increased with an increasing value of “\( a \)” (attractive parameter) but affected to a very limited extent by the value of “\( b \)” (repulsive parameter). This finding is in accordance with the previous conclusion that the phase behaviour of liquids are dominated by the intermolecular attractive forces rather than
Figure 2.7 Calculated C_8H_{18} bulk phase pressure as well as radial and axial pressures (in dimensionless) in nanopores at \( V_r = 1.5 \) and \( T_r = 0.1 - 0.9 \).
the repulsive forces (Temperley, 1947).

The modified EOS model with the improved correlations for predicting the shifts of critical temperature and pressure is applied to calculate the phase properties of the $iC_4$–$nC_4$–$C_8$ system as well as the live light crude oil B–CO$_2$ system in nanopores, which is an extension from the above-mentioned pure component to mixture systems. Tables 2.2a and b list the liquid and vapour compositions before and after flash calculations for the $iC_4$–$nC_4$–$C_8$ system at two different conditions (i.e., constant pressure and constant temperature) from the literature (Wang et al., 2014) and the modified EOS model. The calculated results from the proposed model match well with the measured data in terms of the liquid and vapour compositions and fractions as well as the capillary pressures in nanopores. Some detailed analyses can be found in the previous studies (Wang et al., 2014; Zhang et al., 2017b). Overall, the calculated phase properties from the modified EOS model agree well with the literature results so that the proposed model is effectively validated. In Figure 2.8, the literature recorded (Teklu et al., 2014b) and calculated bubble point pressures of the live light crude oil B–CO$_2$ system versus the pore radius are plotted. The calculated bubble point pressures agree well with the recorded results at the same conditions in the literature. The bubble point pressure is decreased with the reduction of the pore radius, especially when the pore radius is smaller than 100 nm. These findings are in good agreement with the literature results (Zhang et al., 2017b). On the other hand, the modified EOS model considering the shifts of critical properties and capillary pressure presents a similar overall phase behaviour pattern from the improved vdW-EOS, which only takes into account the shifts of critical properties. It means that the shifts of critical properties are the dominate factors affecting phase changes from bulk phase to nanopores.
Figure 2.8 Recorded (Teklu et al., 2014b) and calculated bubble point pressure ($P_b$) of the live light crude oil B–CO$_2$ system at the pore radii of 4–1,000 nm from the modified equation of state and diminishing interface method (Zhang et al., 2017b).
2.5 Summary

In this chapter, a semi-analytical nanoscale-extended EOS, which considers the capillary pressure and critical shifts, is developed to calculate and evaluate the phase behavior of confined pure/mixing fluids in nanopores. The proposed model has been proven to calculate the phase behaviour of confined pure and mixing fluids, even some high carbon number hydrocarbons, in an accurate and efficient manner. The negative pressure state is proven to be physically meaningful for the liquid phase, whose upper temperature limit is quantitatively determined and found to be lowered with the reduction of the pore radius. It is also validated that the phase behaviour of the liquid is dominated by the intermolecular attractive forces. In addition, two modified correlations are proposed to accurately predict the shifts of critical properties. The critical temperature and pressure of confined fluids are decreased with the reduction of pore radius to some certain extent (i.e., \( \frac{\sigma}{r_p} = 0.1 \)). The shifts of critical properties are more important and dominate the changes of phase behaviour for confined fluids in comparison with the influences of the increased capillary pressure from bulk phase to nanopores.
CHAPTER 3  NANOSCALE-EXTENDED ALPHA FUNCTIONS

3.1  Introduction

Cubic equations of state (EOS) are widely applied in academic research and industrial applications due to their simplicity and accuracy for predicting pure and mixing fluid phase and thermodynamic properties in vapour and liquid phases (Abbott, 1973; Lopez-Echeverry et al., 2017; Patel and Teja, 1982; Su et al., 2017; Zhang et al., 2018c). Since the well-known van der Waals (vdW) EOS was initiated in 1873 (Van der Waals, 1910), numerous cubic EOSs have been proposed for the thermodynamic equilibrium calculations during the past one and half centuries, such as the Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK), and Peng–Robinson (PR) EOSs and others (Peng and Robinson, 1976; Redlich and Kwong, 1949; Soave, 1972).

The capacity of these EOSs in calculating the pure and mixing phase properties largely depends on the appropriate selections of alpha functions (Neau et al., 2009a, 2009b; Privat et al., 2015; Twu et al., 1991). The alpha functions in the cubic EOS play important roles in accurately predicting the characteristics of a real pure component deviated from its ideal behaviour (Li and Yang, 2010). In principle, the existing alpha functions can be divided into two categories: Soave- and exponential-type alpha functions. A remarkable success in the alpha function development was achieved by Soave’s work (Soave, 1972). The original Soave alpha function was developed with respect to the acentric factors, which makes it possible to adequately correlate the phase behaviour of pure and mixing fluids containing non-polar or slightly polar components (Mahmoodi and Sedigh, 2017a, 2016). However, a major limitation of the Soave alpha function comes from its abnormal extrema at the
supercritical region, where the attractive function performs a concave upward parabola and
does not decrease monotonically with the temperature increases. Many efforts had been
made to modify the original Soave alpha function and overcome its inherent limitations
(Mathias, 1983; Mathias and Copeman, 1983; Segura et al., 2003; Stryjek and Vera, 1986).
However, some further modifications usually introduced some new deviation terms while
the inherent limitation remains. Later, the exponential-type alpha function, which
demonstrates an asymptotic behaviour when the reduced temperature is approaching
infinity, was proposed by Heyen (Heyen, 1981) and further modified by Trebble and
Bishnoi (Trebble and Bishnoi, 1987) as well as Twu et al. (Twu et al., 1995). Recently, a
series of consistency tests for the alpha functions of the cubic EOSs were conducted and
presented (Le Guennec et al., 2016). Overall, the following three basic conditions are
required for the alpha functions: 1. the alpha function must be finite and positive at all
temperatures; 2. the alpha function equals to the unity at the critical point; 3. The alpha
function approaches a finite value as the temperature becomes infinity (Hernández-
Garduza et al., 2002). The three requirements can be easily satisfied if the Soave-
and
exponential-type alpha functions are utilized concurrently. Although numerous alpha
functions have been developed and/or modified in the past decades, all existing alpha
functions are for the bulk phase case while no work has been developed for the phase
properties of confined fluids in nanopores.

In recent years, confined fluids in porous media, especially in the nanoscale spaces,
attract more attentions due to its wide and practical applications. More specifically,
capillary pressures become considerably large (Nojabaei et al., 2013), critical properties of
the confined fluids shift to different extent (Zhang et al., 2018a), molecule–molecule and
molecule–wall interactions are enhanced (Travalloni et al., 2014; Zarragoicoechea and Kuz, 2002), all of which are resulted from the strong confinement effects and could cause substantial changes in terms of the thermodynamic phase properties at small pore radius. The solubility parameter and minimum miscibility pressure (MMP), which is defined as the lowest operating pressure at which the oil and gas phases can become miscible in any portions at an oil reservoir temperature (Zhang and Gu, 2015), are significantly decreased with the reduction of the pore radius (Zhang et al., 2018b; Zhang et al., 2017b). At the current stage that the experimental approaches are incapable of fully exploring the nanoscale phase properties, the modified EOS coupled with nanoscale-extended alpha functions are necessarily and immediately required.

In this chapter, two new nanoscale-extended alpha functions in the Soave and exponential types are developed by considering the confinement effects, which are applied to calculate the thermodynamic and phase properties of pure and mixing confined fluids in bulk phase ($r_p = 1000$ nm) and nanopores by coupling with a modified SRK EOS. It should be noted that $r_p = 1000$ nm is assumed to be the bulk phase as a result of a series of trial tests, where $r_p = 10,000$, $100,000$, and $1,000,000$ nm have been also used for the calculations and their results are almost equivalent to those at $r_p = 1,000$ nm. On the other hand, some previous studies have validated that the phase behavior at $r_p > 100$ nm are similar to the bulk phase cases (Zhang et al., 2018a; Zhang et al., 2017b, 2017a). The modified SRK EOS is developed by following the similar theoretical manner of the modified vdW EOS in the previous study (Zhang et al., 2018a). The calculated phase and thermodynamic properties from the new models are compared to and validated with the measured data in bulk phase and nanopores. Moreover, a new method is proposed and
verified to determine the nanoscale acentric factors. A series of important parameters, which are the minimum reduced temperature, nanoscale acentric factor, alpha functions and their first and second derivatives, are specifically studied to analyze their behaviour at different temperatures and pore radii. Finally, the original and nanoscale-extended alpha functions in Soave and exponential types are compared and evaluated in terms of the thermodynamic and phase property calculations in bulk phase and nanopores.

3.2 Materials

In this study, pure CO₂, N₂, and a series of alkanes from C₁–C₁₀ are used, whose critical properties (i.e., temperature, pressure, and volume), SRK EOS constants, and Lennard-Jones potential parameters are summarized (Sharma and Sharma, 1977; Whitson and Brule, 2000; Yu and Gao, 2000) and listed in Table 3.1. The pressure–volume–temperature (PVT) tests of the C₈H₁₈–CH₄ system were conducted at T = 311.15 K and the pore radii of rₚ = 3.5 and 3.7 nm (i.e., silica-based mesoporous materials SBA-15 and SBA-16) (Cho et al., 2017). Furthermore, the PVT tests for the N₂–n-C₄H₁₀ system were conducted by using a conventional PVT apparatus connected to a high-temperature and pressure container with a shale coreplug at the temperatures of T = 299.15 and 324.15 K (Y. Liu et al., 2018). It should be noted that the shale coreplug was hydrocarbon-wetting and its dominant pore radius was around 5 nm, which is applied for the subsequent calculations in this study. The purities of N₂ and n-C₄H₁₀ used in the experiments equal to 99.998% and 99.99%, respectively. In addition, the measured phase properties of a ternary hydrocarbon mixture systems of 4.53 mol.% n-C₄H₁₀ + 15.47 mol.% i-C₄H₁₀ + 80.00 mol.% C₈H₁₈ (Wang et al., 2014) are applied to verify the newly-developed model with the nanoscale-extended alpha functions. The detailed experimental set-up and procedures for conducting the above-
Table 3.1

Recorded critical properties (i.e., temperature, pressure, and volume), Soave–Redlich–Kwong equation of state (EOS) constants, and Lennard-Jones potential parameters of CO₂, N₂, O₂, Ar, and C₁–C₁₀ (Sharma and Sharma, 1977; Whitson and Brule, 2000; Yu and Gao, 2000).

<table>
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<th>Component</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (Pa)</th>
<th>( V_c ) (m³/mol)</th>
<th>( a_c ) (Pa·m⁶/mol²)</th>
<th>( b ) (m³/mol)</th>
<th>( \delta k ) (K)</th>
<th>( \sigma ) (m)</th>
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<td>226</td>
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</table>

43
mentioned PVT tests can be referred in the literature (Cho et al., 2017; Y. Liu et al., 2018; Wang et al., 2014; Zhang and Gu, 2016b).

3.3 Theory

3.3.1 Modified equations of state

The conventional SRK EOS is modified to consider the confinement-induced effects of pore radius and molecule–molecule interactions in nanopores. The SRK EOS is one of the most commonly-accepted and widely-used cubic EOS which are usually capable of accurately predicting the vapour–liquid equilibrium (VLE) and fluid stability/metastability (Soave, 1972; van der Waals Interactions, 2009; Van der Waals, 1910; Wang and Gmehling, 1999). Suppose that a nanoscale pore system, as shown in Figure 3.1, consists of some confined particles via the Lennard–Jones potential. The canonical partition function from the statistical thermodynamics is shown as follows (Abrams and Prausnitz, 1975),

$$Q(N,V,T) = \sum_{i} e^{-\frac{E_{i}(N,V)}{RT}} \frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^{N} Z(N,V,T)$$

(3.1)

where $N$ is the number of molecules; $V$ is the total volume; $T$ is the temperature; $E$ is the overall energy state; $k$ is the Boltzmann constant; $\Lambda$ is the de Broglie wavelength,

$$\Lambda = (\frac{h^2}{2\pi mkT})^{0.5}$$

$h$ is the Planck’s constant, $m$ is the molecular mass; $q_{\text{int}}$ is the internal partition function; and $Z$ is the configuration partition function, which is expressed as,

$$Z(N,V,T) = \int e^{-\frac{U(r_1, r_2, ..., r_N)}{kT}} dr_1 dr_2 ... dr_N$$

(3.2)

where $U$ is the potential energy of entire system of $N$ number of molecules which positions are described by $r_i$, $i = 1, 2, ... N$, and $r_i$ is the distance of separation between molecules.
The detailed analytical derivations of the canonical partition function can be found in the previous study (Zhang et al., 2018a), so the pressure is expressed as,

\[
P(N, V, T) = kT \frac{\partial \ln[(V - N\beta)^N e^{\frac{T}{kT} E_{conf}(N, V, T)}]}{\partial V}
\]

\[
= \frac{NkT}{V - N\beta} - \frac{\partial E_{conf}(N, V, T)}{\partial V}
\]

where \( \beta \) is the excluded volume per fluid molecule and \( g(r; \rho, T) \) is the pair correlation function for molecules interacting through the potential \( U(r) \). \( E_{conf}(N, V, T) \) is expressed as (Zhang et al., 2018a),

\[
E_{conf} = \frac{kTn^2C}{2V^2} \int_{r_i > \sigma} U(r_1, r_2, ..., r_N) dV_1 dV_2
\]

Fluid interactions \( U(r) \) are assumed to be numerically represented through the Lennard-Jones potential, whose schematic diagram is shown in Figure 3.1. Then, the integral part of Eq. (3.4) is solved semi-analytically as,

\[
\frac{1}{V} \int \int_{r_i > \sigma} \frac{U(r_1, r_2, ..., r_N)}{kT} dV_1 dV_2 = \frac{4\varepsilon_{11}}{kT} \sigma_{11}^3 f(A_r)
\]

\[
f(A_r) = c_0 + \frac{c_1}{\sqrt{A_r}} + \frac{c_2}{A_r}
\]

where \( A_r \) is the reduced contact area (Zhang et al., 2018a). Accordingly, \( E_{conf}(N, V, T) \) is presented as,

\[
E_{conf} = \frac{-an^2C + 2n^2C_1\sigma_{11}^3 \left( \frac{c_1}{\sqrt{A_r}} + \frac{c_2}{A_r} \right)}{nb \ln \left( \frac{V}{V + nb} \right)}
\]
Figure 3.1 Schematic diagrams of the nanopore network and its associated potential.
where $\epsilon_{LJ}$ is the molecule–molecule Lennard–Jones energy parameter and and $\sigma_{LJ}$ is the molecule–molecule Lennard–Jones size parameter. The modified SRK EOS for the confined fluids in nanopores are obtained by substituting Eq. (3.6) into Eq. (3.3) with a specific $C$ (Travalloni et al., 2014), whose molar base formulation (i.e., divided by the mole number) is shown as follows,

$$P_{NP-SRK} = \frac{RT}{v-b} - \frac{\alpha_T}{v(v+b)}\left[a_c - 2\epsilon_{LJ}\sigma_{LJ}^3 \cdot \left(\frac{c_1}{\sqrt{A_t}} + \frac{c_2}{A_t}\right)\right]$$  \hspace{1cm} (3.7)

where $\alpha_T$ is the so-called $\alpha$ function. Eq. 3.7 is the modified SRK EOS for calculating the phase behavior of pure and mixing confined fluids in nanopores.

### 3.3.2 Critical properties in nanopores

The critical temperature and pressure of the confined fluids in nanopores can be solved at the condition of $(\frac{\partial P}{\partial V})_T = (\frac{\partial^2 P}{\partial V^2})_T = 0$, which are derived from the modified SRK EOS in Eq. 3.7 and shown below, respectively,

$$T_{c_p-SRK} = \frac{3(\sqrt{2} - 1)^2 \cdot \alpha_T}{bR} \left[a_c - 2\epsilon_{LJ}\sigma_{LJ}^3 \cdot \left(\frac{c_1}{\sqrt{A_t}} + \frac{c_2}{A_t}\right)\right]$$  \hspace{1cm} (3.8a)

$$P_{c_p-SRK} = \frac{(\sqrt{2} - 1)^3 \cdot \alpha_T}{b^2} \left[a_c - 2\epsilon_{LJ}\sigma_{LJ}^3 \cdot \left(\frac{c_1}{\sqrt{A_t}} + \frac{c_2}{A_t}\right)\right]$$  \hspace{1cm} (3.8b)

where $T_{c_p}$ and $P_{c_p}$ are the respective critical temperature and pressure in nanopores. It is well known that the corresponding bulk fluid critical properties from the conventional SRK EOS are: $T_{c-SRK} = \frac{3(\sqrt{2} - 1)^2}{bR} a_c$ and $P_{c-SRK} = \frac{(\sqrt{2} - 1)^3}{b^2} a_c$. Hence, the shifts of critical temperature and pressure in nanopores from the SRK EOS are shown as follows,
The equations for calculating the critical shifts in Eqs. (3.9a) and (3.9b) are considered to be general/universal since they are equivalent to those from the modified vdW EOS in the previous study (Zhang et al., 2018a).

3.3.3 Nanoscale acentric factors

Acentric factor (\(\omega\)) is an empirical parameter reflecting the deviation of acentricity or non-sphericity of a compound molecule from that of a simple fluid (e.g., argon or xenon) (Passut and Danner, 1973), which was originally introduced by Pitzer et al. (Li and Yang, 2010; Whitson and Brule, 2000) and modified by incorporating the shifts of the critical properties in nanopores as follows,

\[
\omega = -\log(P_{r\text{-NP}})_{T_r\text{,NP}=0.7} - 1
\]  

\[
P_{r\text{-NP}} = \frac{P_r}{P_{cp}}, \quad T_{r\text{-NP}} = \frac{T}{T_{cp}}
\]

where \(P_{r\text{-NP}}\) is the reduced pressure in nanopores, \(T_{r\text{-NP}}\) is the reduced temperature in nanopores, and \(P_c\) is the vapour pressure. The acentric factor defined at the reduced temperature of \(T_r = 0.7\) has been validated to be accurate for the substances like CO\(_2\) and alkanes of C\(_{1-10}\) (Whitson and Brule, 2000), which still used in nanopores because the reduced temperature is a dimensionless parameter.

The logarithm reduced pressures of the CO\(_2\) and alkanes of C\(_{1-10}\) are calculated at different reduced temperatures, which are plotted versus the reciprocal of the reduced
temperatures in nanopores (i.e., $1/T_{r,NP}$). Figure 3.2 shows a sample that the calculated logarithm reduced pressures for CO$_2$, N$_2$, and alkanes of C$_{1-10}$ at the pore radius of $r_p = 1$ nm are plotted with respect to the reciprocal of the reduced temperatures. Therein, the calculated logarithm reduced pressures at $1/T_{r,NP} = 1.429$ (i.e., $T_{r,NP} = 0.7$) are applied to calculate the nanoscale acentric factors in Eq. 3.10. It can be anticipated that the acentric factors are various at different pore radii because the critical temperatures and pressures are dependent on the pore radius. The logarithm reduced pressures of the CO$_2$ and alkanes of C$_{1-10}$ are calculated at different pore radii of $r_p = 1$–10000 nm and plotted versus the the reciprocal of the reduced temperatures, by means of which the acentric factors at different pore radii are determined. The determined acentric factors for the CO$_2$, N$_2$, O$_2$, Ar, C$_{1-10}$, C$_{12}$, C$_{14}$, C$_{16}$, C$_{18}$, and C$_{19}$ in bulk phase are listed and compared with the measured data in Table 3.2. It is found that the calculated acentric factors agree well with the measured results, whose absolute average deviations are in the range of 0.83–22.07%.

### 3.3.4 Modified alpha functions in nanopores

For a thermodynamic phase equilibrium, the alpha function takes account of the attractivities between the molecules, which depends on the reduced temperature ($T_r$) and acentric factor ($\omega$). As aforementioned that the existing alpha functions can be divided into two categories: Soave-type ($\alpha_{S,T}$) and exponential-type ($\alpha_{E,T}$) functions. Two typical alpha functions in these two categories have been validated for the polar or non-polar non-hydrocarbons and light hydrocarbons (Gasem et al., 2001; Segura et al., 2003), which are extended for the nanoscale calculations by substituting the above-mentioned modified parameters and shown as,
Figure 3.2a Calculated logarithm reduced pressures for CO₂, N₂, and alkanes of C₁⁻₁₀ at the pore radius of \( r_p = 1 \) nm with respect to the reciprocal of the reduced temperatures.
Figure 3.2b Calculated logarithm reduced pressures for CO2, N2, and alkanes of C1–10 at the pore radius of \( r_p = 1 \) nm with respect to the reciprocal of the reduced temperatures.
Table 3.2

Measured (Li and Yang, 2010) and calculated acentric factors for the CO$_2$, N$_2$, O$_2$, Ar, C$_1$–C$_{19}$ in bulk phase.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\omega^m$</th>
<th>$\omega^c$</th>
<th>AAD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.2238</td>
<td>0.2174</td>
<td>2.86</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.0371</td>
<td>0.0311</td>
<td>16.17</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.0222</td>
<td>0.0200</td>
<td>9.91</td>
</tr>
<tr>
<td>Ar</td>
<td>−0.0031</td>
<td>−0.0027</td>
<td>12.90</td>
</tr>
<tr>
<td>C$_1$</td>
<td>0.0080</td>
<td>0.0071</td>
<td>11.25</td>
</tr>
<tr>
<td>C$_2$</td>
<td>0.0989</td>
<td>0.0917</td>
<td>7.28</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0.1520</td>
<td>0.1405</td>
<td>7.57</td>
</tr>
<tr>
<td>C$_4$</td>
<td>0.1978</td>
<td>0.1893</td>
<td>4.30</td>
</tr>
<tr>
<td>C$_5$</td>
<td>0.2501</td>
<td>0.2281</td>
<td>8.80</td>
</tr>
<tr>
<td>C$_6$</td>
<td>0.2988</td>
<td>0.2869</td>
<td>3.98</td>
</tr>
<tr>
<td>C$_7$</td>
<td>0.3486</td>
<td>0.3457</td>
<td>0.83</td>
</tr>
<tr>
<td>C$_8$</td>
<td>0.3971</td>
<td>0.4045</td>
<td>1.86</td>
</tr>
<tr>
<td>C$_9$</td>
<td>0.4442</td>
<td>0.4633</td>
<td>4.30</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>0.5381</td>
<td>0.5221</td>
<td>2.97</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>0.5757</td>
<td>0.6397</td>
<td>11.12</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>0.6442</td>
<td>0.7573</td>
<td>17.56</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>0.7167</td>
<td>0.8749</td>
<td>22.07</td>
</tr>
<tr>
<td>C$_{18}$</td>
<td>0.8160</td>
<td>0.9925</td>
<td>21.63</td>
</tr>
<tr>
<td>C$_{19}$</td>
<td>0.8624</td>
<td>1.0513</td>
<td>21.90</td>
</tr>
</tbody>
</table>

$m$ Measured acentric factors

$c$ Calculated acentric factors
\[\alpha_{T-S-NP} = [1 + m_{S-NP}(1 - \sqrt{T_{r-NP}})]^2 \quad (3.11a)\]

\[m_{S-NP} = 0.480 + 1.574 \omega_{NP} - 0.176 \omega_{NP}^2\]

\[\alpha_{T-E-NP} = \exp[(2 + 1.0444 T_{r-NP}) \cdot (1 - T_{r-NP}^{m_{E-NP}})] \quad (3.11b)\]

\[m_{E-NP} = 0.15683 + 0.51494 \omega_{NP} - 0.054124 \omega_{NP}^2\]

Eqs. 3.11a and b are the new nanoscale-extended Soave and exponential alpha functions.

It should be noted that the constants in Eq. 3.11b are updated for the SRK EOS through the vapor pressure minimization of 36 pure components.

### 3.3.5 Vapour–liquid equilibrium calculations

The VLE calculations, whose detailed steps are specified in Section 2.3.2, based on the modified SRK EOS require a series of iterative computations through, for example, the Newton–Raphson method. The calculated vapour pressures for the CO\(_2\), N\(_2\), O\(_2\), Ar, and C\(_1\)–C\(_{10}\) in bulk phase are listed and compared with measured results in Table 3.3.

### 3.3.6 Enthalpy of vaporization and heat capacity

The new nanoscale-extended alpha functions in Eqs. 3.11a and b are required to be validated by comparing with the experimental measured or literature recorded thermodynamic properties. Some common thermodynamic properties in bulk phase may not be available in nanopores. Here, the enthalpy of vapourization is selected for the validation purpose because of its data availability in nanopores. The fundamental enthalpy thermodynamic formula on a molar scale is shown as,

\[H(T, P) - H^{IG}(T, P) = RT(Z - 1) + \int_{V \rightarrow V(T, P)} [T(\frac{\partial P}{\partial T})_V - P]dV \quad (3.12)\]

By substituting the modified SRK EOS in Eq. 3.7, Eq. 3.12 is rearranged to be,
Table 3.3

Calculated vapour pressures for the CO$_2$, N$_2$, O$_2$, Ar, and C$_1$–C$_{10}$ in bulk phase from the literature (Li and Yang, 2010; Mahmoodi and Sedigh, 2016) and vapour–liquid equilibrium model coupled with the new nanoscale-extended equation of state and alpha functions.

<table>
<thead>
<tr>
<th>Component</th>
<th>$T_r$</th>
<th>$P_v^m$ (kPa)</th>
<th>NDP</th>
<th>AAD (%)</th>
<th>exp (Li and Yang, 2010; Mahmoodi and Sedigh, 2016)</th>
<th>M-Soave</th>
<th>M-exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.714–1.000</td>
<td>530.33–7386.59</td>
<td>65</td>
<td>0.27</td>
<td>0.18</td>
<td>0.45</td>
<td>0.28</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.500–1.000</td>
<td>12.52–3400.20</td>
<td>77</td>
<td>0.75</td>
<td>0.20</td>
<td>0.88</td>
<td>0.67</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.420–1.000</td>
<td>0.15–5043.00</td>
<td>32</td>
<td>2.05</td>
<td>1.20</td>
<td>1.37</td>
<td>1.89</td>
</tr>
<tr>
<td>Ar</td>
<td>0.556–1.000</td>
<td>68.95–4860.52</td>
<td>67</td>
<td>0.87</td>
<td>0.43</td>
<td>1.03</td>
<td>1.12</td>
</tr>
<tr>
<td>C$_1$</td>
<td>0.476–1.000</td>
<td>11.70–4596.09</td>
<td>48</td>
<td>0.67</td>
<td>0.67</td>
<td>1.24</td>
<td>1.55</td>
</tr>
<tr>
<td>C$_2$</td>
<td>0.780–1.000</td>
<td>912.99–4863.50</td>
<td>30</td>
<td>0.34</td>
<td>0.45</td>
<td>0.22</td>
<td>0.76</td>
</tr>
<tr>
<td>C$_3$</td>
<td>0.698–1.000</td>
<td>291.79–4239.31</td>
<td>34</td>
<td>0.26</td>
<td>0.43</td>
<td>0.31</td>
<td>0.28</td>
</tr>
<tr>
<td>C$_4$</td>
<td>0.753–1.000</td>
<td>456.65–3796.02</td>
<td>48</td>
<td>0.36</td>
<td>0.68</td>
<td>0.59</td>
<td>0.83</td>
</tr>
<tr>
<td>C$_5$</td>
<td>0.745–1.000</td>
<td>338.78–3369.00</td>
<td>25</td>
<td>0.25</td>
<td>0.52</td>
<td>0.47</td>
<td>1.03</td>
</tr>
<tr>
<td>C$_6$</td>
<td>0.581–1.000</td>
<td>17.31–3020.00</td>
<td>54</td>
<td>0.70</td>
<td>1.46</td>
<td>0.66</td>
<td>0.71</td>
</tr>
<tr>
<td>C$_7$</td>
<td>0.687–1.000</td>
<td>99.66–2740.00</td>
<td>49</td>
<td>0.25</td>
<td>0.77</td>
<td>0.34</td>
<td>0.64</td>
</tr>
<tr>
<td>C$_8$</td>
<td>0.632–1.000</td>
<td>29.04–2486.00</td>
<td>25</td>
<td>0.52</td>
<td>1.03</td>
<td>0.71</td>
<td>1.00</td>
</tr>
<tr>
<td>C$_9$</td>
<td>0.607–1.000</td>
<td>13.24–2305.00</td>
<td>20</td>
<td>0.80</td>
<td>0.69</td>
<td>0.68</td>
<td>0.72</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>0.528–1.000</td>
<td>0.87–2110.00</td>
<td>94</td>
<td>3.84</td>
<td>5.03</td>
<td>1.17</td>
<td>1.68</td>
</tr>
<tr>
<td>AAD (%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.85</td>
<td>0.98</td>
<td>0.72</td>
<td>0.94</td>
</tr>
<tr>
<td>MAD (%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3.84</td>
<td>5.03</td>
<td>1.37</td>
<td>1.89</td>
</tr>
</tbody>
</table>

$m$ experimentally measured
NDP number of data point
AAD average absolute deviation
MAD maximum absolute deviation
\[ H(T, P) - H^G(T, P) = RT(Z - 1) + \frac{[a_c - 2eLJ\sigma_{LJ}^3 \cdot (\frac{c_1}{A_t} + \frac{c_2}{A_t})] \cdot [-Ta_c \left( \frac{d\alpha_T}{dT} \right) + \alpha_T]}{b} \cdot \ln\left( \frac{V}{V + b} \right) \]

(3.13)

Thus, the enthalpy of vaporization at saturation temperature is expressed as,

\[ \Delta^s_H(T) = RT(Z_v - Z_i) + \frac{[a_c - 2eLJ\sigma_{LJ}^3 \cdot (\frac{c_1}{A_t} + \frac{c_2}{A_t})] \cdot [-Ta_c \left( \frac{d\alpha_T}{dT} \right) + \alpha_T]}{b} \cdot [\ln\left( \frac{Z_v}{Z_v + B} \right) - \ln\left( \frac{Z_i}{Z_i + B} \right)] \]

(3.14)

\[ B = \frac{bP}{RT} \]

The enthalpy of vaporization in nanopores can be determined by means of the nanoscale-extended EOS and alpha functions. By means of the new nanoscale-extended Soave and logarithm alpha functions from Eqs. 3.11a and b, the term of \( \frac{d\alpha_T}{dT} \) can be analytically expressed as follows,

\[ \frac{d\alpha_{T-S-NP}}{dT} = -\frac{m_{S-NP}\left(\sqrt{T_{cp}} + m_{S-NP}(\sqrt{T_{cp}} - \sqrt{T})\right)}{T_{cp} \cdot \sqrt{T}} \]

(3.15a)

\[ \frac{d\alpha_{T-E-NP}}{dT} = \exp\left\{ (2 + 0.836 \frac{T}{T_{cp}}) \cdot [1 - \left( \frac{T}{T_{cp}} \right)^{m_{E-NP}}} \right\} \cdot \left\{ \frac{0.836}{T_{cp}} \cdot [1 - \left( \frac{T}{T_{cp}} \right)^{m_{E-NP}}} - \frac{2m_{E-NP}T_{E-NP}^{m_{E-NP}-1}}{T_{cp}^{m_{E-NP}}} - 0.836m_{E-NP} \cdot \frac{T_{E-NP}}{T_{cp}^{m_{E-NP}+1}} \right\} \]

(3.15b)

Thus, the enthalpies of vaporization for different substances in bulk phase (when pore radius is set to be infinity) and nanopores can be calculated by using Eq. 3.14, which are listed and compared with the measured or recorded data in Table 3.4.

In addition, heat capacity is a measurable physical quantity which equals to the ratio of the heat added to or removed from an object to the resulting temperature changes (Smith,
1950). The constant-pressure \((C_p)\) and volume \((C_V)\) heat capacities are two common quantities, whose thermodynamic formulations are shown as follows,

\[
C_p = -\left[ T \left( \frac{\partial P}{\partial V} \right)^{-1} \left( \frac{\partial P}{\partial T} \right)^2 + R \right] - \frac{T a_c (d^2 \alpha_T)}{b} \ln \left( \frac{V}{V + b} \right) \\
C_V = -\frac{T a_c (d^2 \alpha_T)}{b} \ln \left( \frac{V}{V + b} \right)
\]

(3.16a)

(3.16b)

It is clearly from the above two equations that the constant-pressure and constant-volume heat capacities can be determined once the second derivatives of \(\alpha\) function to the temperature are given. Thus, the analytical formulations of the second derivatives of \(\alpha\) function to the temperature are shown,

\[
\frac{d^2 \alpha_{T-S-NP}}{dT^2} = \frac{m_{S-NP} (1 + m_{S-NP})}{2 \sqrt{T_{cp}} \cdot T_{cp}^2}
\]

\[
\frac{d^2 \alpha_{T-E-NP}}{dT^2} = \exp \left\{ (2 + 0.836) \frac{T}{T_{cp}} \left[ 1 - \left( \frac{T}{T_{cp}} \right)^{m_{E-NP}} \right] \right\} \cdot \frac{0.836}{T_{cp}} \cdot \left[ 1 - \left( \frac{T}{T_{cp}} \right)^{m_{E-NP}} \right] \cdot \left(2 + 0.836 \frac{T}{T_{cp}} \right) \cdot \left(-m_{E-NP} \right) \cdot \\
\left( \frac{T}{T_{cp}} \right)^{m_{E-NP}} \cdot \left( \frac{T}{T_{cp}} \right) \cdot \left[ 1 - \left( \frac{T}{T_{cp}} \right)^{m_{E-NP}} \right] \cdot \frac{2 m_{E-NP} T_{cp}^{m_{E-NP}}}{T_{cp}^{m_{E-NP}+1}} \cdot \left(1 - \frac{T}{T_{cp}} \right)^{m_{E-NP}} \cdot \\
\left[- \frac{0.836 m_{E-NP} T_{cp}^{m_{E-NP}-1}}{T_{cp}^{m_{E-NP}+1}} - \frac{2 m_{E-NP} \cdot (m_{E-NP} - 1) T_{cp}^{m_{E-NP}-2}}{T_{cp}^{m_{E-NP}+1}} - \frac{0.836 m_{E-NP}^2 T_{cp}^{m_{E-NP}-1}}{T_{cp}^{m_{E-NP}+1}} \right]
\]

(3.17b)

The constant-pressure heat capacities of different components are calculated from the above-mentioned equations, which are listed and compared with the measured or recorded data in Table 3.4. It is worthwhile to mention that the newly-developed nanoscale-extended EOS and alpha functions can also be applicable for the bulk phase calculations when the pore radius is set to be large enough.
Table 3.4

Measured (Li and Yang, 2010; Neau et al., 2009a, 2009b) and calculated enthalpies of vaporization and constant pressure heat capacities for the CO$_2$, N$_2$, O$_2$, Ar, and C$_1$–C$_{10}$ in bulk phase from the new nanoscale-extended equation of state and $\alpha$ functions.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\Delta^f H$ (T (K))</th>
<th>AAD (%)</th>
<th>$C_p$ (T (K))</th>
<th>AAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NDP</td>
<td>Soave</td>
<td>Exp</td>
<td>M-Soave</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>244.3–303.7</td>
<td>56</td>
<td>5.21</td>
<td>5.32</td>
</tr>
<tr>
<td>N$_2$</td>
<td>63.2–110.0</td>
<td>7</td>
<td>0.85</td>
<td>0.32</td>
</tr>
<tr>
<td>O$_2$</td>
<td>54.4–150.0</td>
<td>11</td>
<td>1.97</td>
<td>1.82</td>
</tr>
<tr>
<td>Ar</td>
<td>83.8–150.0</td>
<td>8</td>
<td>3.24</td>
<td>3.21</td>
</tr>
<tr>
<td>C$_1$</td>
<td>90.7–190.0</td>
<td>11</td>
<td>3.83</td>
<td>4.44</td>
</tr>
<tr>
<td>C$_2$</td>
<td>90.4–300.0</td>
<td>12</td>
<td>2.36</td>
<td>2.33</td>
</tr>
<tr>
<td>C$_3$</td>
<td>85.5–360.0</td>
<td>15</td>
<td>2.46</td>
<td>1.53</td>
</tr>
<tr>
<td>C$_4$</td>
<td>260.0–428.0</td>
<td>24</td>
<td>1.68</td>
<td>1.16</td>
</tr>
<tr>
<td>C$_5$</td>
<td>149.0–303.0</td>
<td>24</td>
<td>5.65</td>
<td>12.18</td>
</tr>
<tr>
<td>C$_6$</td>
<td>183.0–493.0</td>
<td>54</td>
<td>2.01</td>
<td>1.99</td>
</tr>
<tr>
<td>C$_7$</td>
<td>340.0–480.0</td>
<td>6</td>
<td>1.21</td>
<td>0.77</td>
</tr>
<tr>
<td>C$_8$</td>
<td>360.0–500.0</td>
<td>6</td>
<td>5.67</td>
<td>4.87</td>
</tr>
<tr>
<td>C$_9$</td>
<td>247.0–460.0</td>
<td>41</td>
<td>1.53</td>
<td>1.75</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>247.0–460.0</td>
<td>41</td>
<td>5.48</td>
<td>14.03</td>
</tr>
<tr>
<td>AAD (%)</td>
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<td>–</td>
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<td>2.05</td>
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<tr>
<td>Mad (%)</td>
<td>–</td>
<td>–</td>
<td>5.21</td>
<td>5.32</td>
</tr>
</tbody>
</table>

| NDP | Number of data point |
| AAD | Average absolute deviation |
| MAD | Maximum absolute deviation |
3.4 Results and discussion

3.4.1 Model verifications

The proposed VLE model, which is on a basis of the modified SRK EOS and coupled with two new nanoscale-extended alpha functions (i.e., M-Soave and M-exponential), is applied to calculate a series of phase and thermodynamic properties in bulk phase and nanopores.

The calculated vapour pressures for the CO$_2$, N$_2$, O$_2$, Ar, and C$_1$–C$_{10}$ in bulk phase from the new nanoscale-extended SRK EOS and alpha functions are listed in Table 3.3, which are compared with the experimentally measured data and calculated results from the Peng–Robinson EOS (PR EOS) coupled with original Soave and exponential alpha functions at different temperatures from the literature (Li and Yang, 2010; Mahmoodi and Sedigh, 2016; Neau et al., 2009a, 2009b). It is found that both the PR EOS coupled with the original alpha functions and the modified SRK EOS coupled with the nanoscale-extended alpha functions are capable of accurately predicting the vapour pressures in bulk phase. The proposed models in this study provide more accurate vapour pressures with overall percentage average absolute deviations (AAD%) of 0.72% (M-Soave) and 0.94% (M-exp) and maximum absolute deviations (MAD%) of 1.37% and 1.89% compared with the experimentally measured data, which are better than those from the previous studies with overall AAD% of 0.85% and 0.98% and MAD% of 3.84% and 5.03%. Furthermore, the enthalpies of vaporization and constant-pressure heat capacities for the CO$_2$, N$_2$, O$_2$, Ar, and C$_1$–C$_{10}$ in bulk phase are calculated from the modified SRK EOS coupled with the M-Soave and M-exp alpha functions and listed in Table 3.4. In comparison with the calculated results from the previous studies, the newly-proposed models perform better in the
constant-pressure heat capacity with overall AAD% of 7.77% and 10.71% and MAD% of 13.45% and 19.76% but become comparable in the enthalpy of vaporization calculations. Overall, the nanoscale-extended SRK EOS and two alpha functions are accurate for calculating the phase and thermodynamic properties in bulk phase.

The new models are better to be verified at the nanometer scale by comparing their results with the experimentally measured data. Figures 3.3a and b show the measured (Angus, 1978) and calculated enthalpies of vaporization and heat capacities for N₂ in bulk phase and nanopores at different temperatures and pore radii, keep in mind that the nanoscale experimental phase and thermodynamic data are extremely scarce currently. It is easily seen from these figures that the calculated enthalpies of vaporization and heat capacities from the nanoscale-extended SRK EOS coupled with the two new alpha functions agree well with the measured thermodynamic data in bulk phase and nanopores. Hence, the newly-developed nanoscale-extended SRK EOS coupled with the two new alpha functions are capable of accurately calculating the phase and thermodynamic properties in bulk phase and nanopores.

3.4.2 Parameter analyses

Minimum reduced temperatures

The alpha functions are a function of the reduced temperature and acentric factor. The temperature-dependent features of the alpha functions are specifically studied here since the acentric factors are normally fixed at a constant pressure and/or pore radius. The first derivatives of the Soave and exponential alpha functions to the reduced temperature are shown as follows,
Figure 3.3a Measured (Angus, 1978) and calculated enthalpies of vaporization for the $\text{N}_2$ from the modified equation of state with the two nanoscale-extended alpha functions at different temperatures in bulk phase and nanopores.
Figure 3.3b Measured (Angus, 1978) and calculated heat capacities for the N$_2$ from the modified equation of state with the two nanoscale-extended alpha functions at different temperatures in bulk phase and nanopores.
\[
\frac{\partial \alpha_{T-S}}{\partial T} = - \frac{m_S[1+m_S(1-\sqrt{T})]}{\sqrt{T}} 
\]  
(3.21a)
\[
\frac{\partial \alpha_{T-E}}{\partial T} = \exp[(2+0.836T)(1-T^{m_e})][\frac{0.836}{T^{m_e}}-\frac{2m_E}{T}-0.836(1+m_E)] 
\]  
(3.21b)

Suppose that Eqs. 3.21a and b infinitely approach zero (please note that the second term is assumed to be zero since the first term right-hand side of Eq. 3.21b won’t be zero) in order to obtain the minimum conditions,

\[
\sqrt{T_{r-min}} = \frac{1+m_S}{m_S} 
\]  
(3.22a)
\[
\frac{0.836}{T_{r-min}^{m_e}}-\frac{2m_E}{T_{r-min}} = 0.836(1+m_E) 
\]  
(3.22b)

The equivalent conditions for Eq. 3.22b can never be satisfied since its left-hand side terms are always larger than the right-hand side terms. Hence, the exponential alpha function is monotonically related with the reduced temperature so that no minimum conditions can be obtained. Eq. 3.22a shows that the minimum conditions for the Soave alpha function can be reached when \(m_S\) is positive. The calculated \(m\) and \(1+m\) in the Soave and exponential types are plotted versus the acentric factors in Figure 3.4a. It is seen from the figure that the \(m_S\) and \(1+m_S\) are always positive at \(\omega > -0.295\). In Figure 3.4b, the ratios of \(1+m_S\) to \(m_S\) (i.e., \(\sqrt{T_{r-min}}\)) are plotted with respect to the acentric factors. It is found from the figure that a vertical asymptote occurs roughly at \(\omega = -0.295\), lower than which the ratios are always negative and become more negative by increasing the acentric factors. On the other hand, the ratios are always positive and decreased or even be a horizontal asymptote (approaching the unity) with the acentric factor at \(\omega > -0.295\). Thus, the minimum reduced
temperature decreases with the acentric factor increases. Cautious should be taken that an increasing acentric factor usually causes the critical properties to be larger so that the minimum reduced temperature reversely increases (Mahmoodi and Sedigh, 2017a).

**Nanoscale acentric factors**

Only the nanoscale acentric factors from the newly-proposed method are specified here since the acentric factors in bulk phase have been extensively introduced in the previous publications. The nanoscale acentric factors of the CO$_2$, N$_2$, and C$_{1-10}$ at the pore radius of 1–1000 nm are determined by means of the new method demonstrated in Figure 3.2, which are plotted versus the pore radius in Figures 3.5a and b. It is found from the figures that the acentric factors are increased with the pore radius reductions. More precisely, the acentric factors remain constant or slightly increase with the pore radius reductions at $r_p \geq 50$ nm while they become quickly increased at $r_p < 50$ nm. As the acentric factors for different components vary in bulk phase, in a similar manner, their behaviour in nanopores are also different. Normally, for alkanes, the acentric factors in bulk phase and nanopore are increased with the carbon number increase. For the twelve components, the acentric factors of the CO$_2$ and C$_{1-10}$ perform similar patterns and are sensitive to the pore radius except that the acentric factors of N$_2$ are slightly insensitive.

**Attractive functions in bulk phase and nanopores**

Figures 3.6 show the calculated Soave and exponential alpha functions and dimensionless attractive term of $A$ (i.e., $A = \frac{a_x \alpha_x P}{(RT)^2}$) for the CO$_2$, N$_2$, and C$_{1-10}$ in bulk phase at different temperatures. The alpha functions in different types perform significantly different. The Soave alpha functions are initially decreased with the temperature increase.
Figure 3.4a Calculated $m$ and $m+1$ from the Soave and exponential type alpha functions from $-0.5$ to 2.
Figure 3.4b Calculated ratios of $m+1$ to $m$ from the Soave type alpha function with respect to the acentric factors from $-0.5$ to $2$. 
Figure 3.5a Calculated acentric factors for CO$_2$, N$_2$, and alkanes of C$_1$–C$_{10}$ at different pore radii of $r_p = 1$–1000 nm.
Figure 3.5b Calculated acentric factors for CO₂, N₂, and alkanes of C₁–C₁₀ at different pore radii of \( r_p = 1–1000 \) nm.
but increase once passing the minimum points, whereas the exponential alpha functions are monotonically decreased with the temperature and asymptotically approach zero. The minimum Soave alpha functions at the supercritical conditions are various for different components that the high carbon-number alkanes reach the minimum conditions at higher temperatures in comparison with those of the low carbon-number alkanes or gaseous components like N\textsubscript{2}. Moreover, at extremely high temperatures (4000 K), the Soave alpha functions of the alkanes are almost equivalent at around 0.5, which is lower than the CO\textsubscript{2} (1.4) and N\textsubscript{2} (2.3) cases. On the other hand, the dimensionless attractive term $A$ are quickly reduced with the temperature at low temperatures and become almost constant afterwards. It should be noted that the $A$ in the Soave and exponential types are equivalent. However, they perform marginally different for different components. In a similar manner with the alpha functions, the $A$ of the CO\textsubscript{2}, N\textsubscript{2} and lighter alkanes like C\textsubscript{1} and C\textsubscript{2} are decreased more quickly with the temperature increase in comparison with those of the higher carbon-number alkanes. Hence, it may be concluded that the attractivities between molecules are reduced with the temperature and become asymptotically to zero when temperatures exceed some certain high values. In addition, the attractivities between the higher carbon-number alkanes are stronger than those of the lighter components.

The Soave alpha functions of the CO\textsubscript{2}, N\textsubscript{2}, and C\textsubscript{1–10} are calculated by means of the new models at the pore radii of 1–1000 nm, which are plotted with respect to the temperatures in Figures 3.7. The Soave alpha functions in nanopores are found to be much different from those in bulk phase but also presented as various concave upward parabola curves with respect to the temperatures. More specifically, the alpha functions at the pore radius of 1000 nm equal to those in bulk phase and become different by reducing the pore
Figure 3.6 Calculated alpha functions in the Soave and exponential types and dimensionless attractive term A for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ in bulk phase at different temperatures.
Figure 3.6 Calculated alpha functions in the Soave and exponential types and dimensionless attractive term A for the (g) C_5; (h) C_6; (i) C_7; (j) C_8; (k) C_9; and (l) C_{10} in bulk phase at different temperatures.
radius. As the pore radii become smaller, both the initial reductions and subsequent increases of the Soave alpha functions become faster, their minimum conditions occur at lower temperatures, and their values at high temperatures are significantly larger. Moreover, the temperature effect on the Soave alpha functions are dependent on the pore radii. For example, in comparison with the CO$_2$ case, the Soave alpha functions of the N$_2$ in bulk phase have a more drastic decrease and increase versus temperatures and a lower temperature for the minimum condition while become less sensitive at $r_p \leq 10$ nm. In a similar manner with that in bulk phase, the CO$_2$, N$_2$, or lighter alkanes like C$_1$ and C$_2$ cases are still sensitive to the temperature increases in nanopores. Furthermore, the alpha function behaviour of the CO$_2$ and alkane cases initiate to be substantially different at $r_p < 50$ nm while that of the N$_2$ case occurs at $r_p < 500$ nm. Thus, it may be concluded that the alpha functions of some components, such as the N$_2$, are sensitive to the temperatures but can be insensitive to the pore radii. For alkanes, their sensitivities of the alpha functions to the temperatures and pore radii are weakened with the carbon number increase. The exponential alpha functions of the CO$_2$, N$_2$, and C$_{1-10}$ in nanopores are much different from those in bulk phase but also decreased monotonically with the temperatures, which are similar to the Soave alpha functions in nanopores and presented in Figure 3.8.

Figures 3.9 and 3.10 show the dimensionless attractive term $A$ in Soave and exponential types for the CO$_2$, N$_2$, and C$_{1-10}$ in nanopores at different temperatures and $r_p = 1–1000$ nm. The calculated $A$ in Soave type from Figure 3.9 are initially reduced with the temperature to the minimum and then reversely increase afterwards, which are similar to the patterns of the Soave alpha functions in nanopores but different from the $A$ vs. temperature curves in bulk phase. The corresponding temperatures for the minimum $A$ in
Figure 3.7 Calculated alpha functions in Soave type for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.7 Calculated alpha functions in Soave type for the (g) C₅; (h) C₆; (i) C₇; (j) C₈; (k) C₉; and (l) C₁₀ at the pore radii of $r_p$ = 1–1000 nm and different temperatures.
Figure 3.9 are the exactly same with those for the minimum alpha functions in Figure 3.7. The values of the $A$ in nanopores are larger than those in bulk phase at most temperatures. It is easily seen from the figures that the apparent differences in terms of the $A$ values for the CO$_2$ and alkanes are initiated at $r_p < 50$ nm and for the N$_2$ case at $r_p < 10$ nm, which can be also observed from the Soave and exponential alpha functions in Figures 3.7 and 3.8 as well as the calculated $A$ in exponential type in Figure 3.10. Overall, the attractive values of the heavier components, such as the intermediate alkanes, become larger than those of the light alkanes like C$_{1-2}$, CO$_2$ and N$_2$.

From Figures 3.7–3.10, the alpha functions in Soave and exponential types always become larger with the reduction of pore radius at most temperatures but may be different at some specific temperatures. Figures 3.11 show the calculated Soave alpha functions for the CO$_2$, N$_2$, and C$_{1-10}$ at $r_p = 1–1000$ nm and $T_r = 0.01, 1, 3,$ and 8. The Soave alpha functions for all the components increase with the pore radius reductions at $T_r = 0.01, 3,$ and 8, whereas they reversely decrease by reducing the pore radius at $T_r = 1$. The similar patterns are also presented from the exponential alpha functions at different temperatures and their specific values with respect to the pore radius at $T_r = 1$ are shown in Figures 3.12. Therefore, it is concluded that in a dissimilar manner with the cases at most temperatures, the alpha functions for the CO$_2$, N$_2$, and C$_{1-10}$ at their critical temperatures (i.e., $T_r = 1$) are decreased with the pore radius reductions.

**First and second derivatives of alpha functions**

The first and second derivatives of the alpha functions to the temperatures (i.e., Eqs. 3.18 and 3.20) are critically important for calculating the thermodynamic properties (Mahmoodi and Sedigh, 2017a, 2016). In this study, the mathematical behaviour of the first
Figure 3.8 Calculated alpha functions in exponential type for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ at the pore radii of $r_p =$ 1–1000 nm and different temperatures.
Figure 3.8 Calculated alpha functions in exponential type for the (g) C\textsubscript{5}; (h) C\textsubscript{6}; (i) C\textsubscript{7}; (j) C\textsubscript{8}; (k) C\textsubscript{9}; and (l) C\textsubscript{10} at the pore radii of \( r_p = 1\text{–}1000 \) nm and different temperatures.
Figure 3.9 Calculated dimensionless attractive term $A$ in Soave type for the (a) CO2; (b) N2; (c) C1; (d) C2; (e) C3; and (f) C4 at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.9 Calculated dimensionless attractive term $A$ in Soave type for the (g) $C_5$; (h) $C_6$; (i) $C_7$; (j) $C_8$; (k) $C_9$; and (l) $C_{10}$ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.10 Calculated dimensionless attractive term $A$ in exponential type for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.10 Calculated dimensionless attractive term $A$ in exponential type for the (g) $C_5$; (h) $C_6$; (i) $C_7$; (j) $C_8$; (k) $C_9$; and (l) $C_{10}$ at the pore radii of $r_p = 1$–$1000$ nm and different temperatures.
and second derivatives of the alpha functions in Soave and exponential types in bulk phase and nanopores are specifically investigated, whose results for the CO₂, N₂, and C₁–10 at different temperatures and/or pore radii are shown in Figures 3.13–3.17. Both the first and second derivatives in Soave and exponential types are continuous with respect to the temperature at \( T \leq 4000 \) K. More specifically, the first derivatives in the two types always increase while the second derivatives reduce with the temperature to different extent in bulk phase and nanopores. Moreover, the respective first derivatives in exponential type and the second derivatives are increased and decreased to be asymptotically approaching zero, whereas the first derivatives in Soave type increase with the temperature from negative to positive. It is obvious that the first and second derivatives for the heavier components are less sensitive to the temperature increases compared to the lighter cases. The first and second derivatives become considerably different at smaller pore radii. In comparison with those at a larger pore radius, the first derivatives in the two types are initially smaller at low temperatures and become larger at high temperatures, the second derivatives in Soave type are always larger, and the second derivatives in exponential type are firstly larger at low temperatures but reduce to be smaller at high temperatures. Furthermore, the first and second derivatives for all the components become more sensitive to the temperatures at smaller pore radii.

### 3.4.3 Comparisons of different alpha functions

The original Soave and exponential alpha functions and their nanoscale-extended formulations are applied for all case calculations aforementioned in bulk phase and nanopores. However, it still remains unclear which one is superior for the bulk phase and nanopore calculations. Table 3.3 lists the calculated vapour pressures for the CO₂, N₂, O₂,
Figure 3.11 Calculated alpha functions in Soave type for CO₂, N₂, and alkanes of C₁–10 at different pore radii of \( r_p = 1–1000 \) nm and reduced temperatures of (a1 and a2) \( T_r = 0.01 \) and (b1 and b2) \( T_r = 1 \).
Figure 3.11 Calculated alpha functions in Soave type for CO₂, N₂, and alkanes of C₁–C₁₀ at different pore radii of \( r_p = 1–1000 \) nm and reduced temperatures of (c₁ and c₂) \( T_r = 3 \) and (d₁ and d₂) \( T_r = 8 \).
Figure 3.12 Calculated alpha functions in exponential type for CO\textsubscript{2}, N\textsubscript{2}, and alkanes of C\textsubscript{1–10} at different pore radii of \( r_p = 1\)–1000 nm and reduced temperatures of \( T_r = 1 \).
Figure 3.13 Calculated first and second derivatives of the alpha functions in the Soave and exponential types with respect to temperatures for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ in bulk phase at different temperatures.
Figure 3.13 Calculated first and second derivatives of the alpha functions in the Soave and exponential types with respect to temperatures for the (g) C₅; (h) C₆; (i) C₇; (j) C₈; (k) C₉; and (l) C₁₀ in bulk phase at different temperatures.
Figure 3.14 Calculated first derivatives of the alpha functions in Soave type with respect to temperatures for the (a) CO₂; (b) N₂; (c) C₁; (d) C₂; (e) C₃; and (f) C₄ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.14 Calculated first derivatives of the alpha functions in Soave type with respect to temperatures for the (g) C₅; (h) C₆; (i) C₇; (j) C₈; (k) C₉; and (l) C₁₀ at the pore radii of \( r_p = 1\)–1000 nm and different temperatures.
Figure 3.15 Calculated first derivatives of the alpha functions in exponential type with respect to temperatures for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.15 Calculated first derivatives of the alpha functions in exponential type with respect to temperatures for the (g) C$_5$; (h) C$_6$; (i) C$_7$; (j) C$_8$; (k) C$_9$; and (l) C$_{10}$ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.16 Calculated second derivatives of the alpha functions in Soave type with respect to temperatures for the (a) CO$_2$; (b) N$_2$; (c) C$_1$; (d) C$_2$; (e) C$_3$; and (f) C$_4$ at the pore radii of $r_p = 1$–1000 nm and different temperatures.
Figure 3.16 Calculated second derivatives of the alpha functions in Soave type with respect to temperatures for the (g) C5; (h) C6; (i) C7; (j) C8; (k) C9; and (l) C10 at the pore radii of \( r_p = 1\text{–}1000 \text{ nm} \) and different temperatures.
Figure 3.17 Calculated second derivatives of the alpha functions in exponential type with respect to temperatures for the (a) CO₂; (b) N₂; (c) C₁; (d) C₂; (e) C₃; and (f) C₄ at the pore radii of \( r_p = 1\text{--}1000 \text{ nm} \) and different temperatures.
Figure 3.17 Calculated second derivatives of the alpha functions in exponential type with respect to temperatures for the (g) C₅; (h) C₆; (i) C₇; (j) C₈; (k) C₉; and (l) C₁₀ at the pore radii of \( r_p = 1–1000 \) nm and different temperatures.
Ar, and C₁–C₁₀ in bulk phase from the four different alpha functions, where the AAD% between the calculated and measured data from the Soave, exponential, M-Soave, and M-exp alpha functions are determined to be 0.85%, 0.98%, 0.72%, and 0.84%, respectively. It seems the M-Soave, M-exp, and original Soave alpha functions are slightly more accurate than the original exponential alpha function for calculating the vapour pressures in bulk phase. Moreover, the calculated enthalpies of vaporization for the same components from the four alpha functions are listed in Table 3.4, whose respective AAD% with the measured data are equal to 2.46%, 2.05%, 2.75%, and 3.21%. Here, the original exponential alpha function performs the best while the other three functions are comparable for the enthalpy of vaporization calculations in bulk phase. On the other hand, the M-Soave alpha function with the AAD% of 7.77% is superior to the other three functions in terms of the constant-pressure heat capacity calculations in bulk phase. Given that their AAD% and MAD% are all small and close to each other, it is hard to determine which alpha function is the best for the phase and thermodynamic properties in bulk phase.

The nanoscale-extended Soave and exponential alpha functions coupled with the modified SRK EOS are applied to calculate the phase behaviour of three mixtures in nanopores. Table 3.5 lists the measured (Wang et al., 2014) and calculated PVT data of the iC₄–nC₄–C₈ mixtures in the micro-channel of 10 μm and nano-channel of 100 nm at the constant pressure and temperature conditions. It is found from the table that the overall performances of the two alpha functions are similar for the phase calculations in nanopores. The application of the M-Soave alpha function performs slightly better in the constant pressure case while the model with the M-exponential case has more accurate results in the constant temperature case. The pressure–volume diagrams of the C₈H₁₈–CH₄ mixtures
from the modified SRK EOS coupled with the two nanoscale-extended alpha functions are calculated at the temperature of $T = 311.15$ K and pore radii of $r_p = 3.5$ and 3.7 nm, which are compared with the measured data (Cho et al., 2017) in Figure 3.18. In Figure 3.19, the measured (Y. Liu et al., 2018) and calculated pressure–volume diagrams of the $\text{N}_2$–$n$-$\text{C}_4\text{H}_{10}$ mixtures at the pore radius of $r_p = 5.0$ nm and different temperatures of $T = 299.15$ and 324.15 K are shown. The calculated results from the two alpha functions are almost equivalent and in reasonable agreement with the measured results for these two mixtures at different conditions in nanopores. Hence, the four alpha functions for the bulk phase calculations and the two nanoscale-extended alpha functions for the nanoscale calculations are validated to be accurate. Some of them may be slightly more accurate for some case calculations but none of them can be a general alpha function which always performs the best for all case calculations in bulk phase or nanopores. Finally, it is worthwhile to mention that the constants of the exponential-type alpha function were determined from the PR EOS perspective and may cause some deviations for the SRK EOS cases. A recent study regarding the SRK-type exponential alpha functions (Mahmoodi and Sedigh, 2017b) was developed, which may be compatible with the proposed models after further validations in the future.
Table 3.5

Measured (Wang et al., 2014) and calculated pressure–volume–temperature data from the modified Soave–Redlich–Kwong (SRK) equation of state with the nanoscale-extended Soave and exponential type alpha functions for \( iC_4–nC_4–C_8 \) system in the micro-channel of 10 μm and nano-channel of 100 nm at (a) constant pressure and (b) constant temperature.

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<th>After flash calculation(^a)</th>
<th>After flash calculation (with M-Soave type)</th>
<th>AAD(^b) (%)</th>
<th>After flash calculation (with M-exp type)</th>
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(a) constant pressure case

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<th>After flash calculation (with M-Soave type)</th>
<th>AAD(^b) (%)</th>
<th>After flash calculation (with M-exp type)</th>
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<td>70.50</td>
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<td>74.74</td>
</tr>
<tr>
<td>IFT (mJ/m(^2))</td>
<td>–</td>
<td></td>
<td></td>
<td>13.33</td>
<td></td>
<td>12.34</td>
</tr>
<tr>
<td>(P_{cap}) in micro-channel (kPa)</td>
<td>–</td>
<td></td>
<td></td>
<td>2.77</td>
<td></td>
<td>1.98</td>
</tr>
<tr>
<td>(P_{cap}) in nano-channel (kPa)</td>
<td>–</td>
<td></td>
<td></td>
<td>235.54</td>
<td></td>
<td>189.44</td>
</tr>
</tbody>
</table>

(b) constant temperature case
Figure 3.18a Measured (Cho et al., 2017) and calculated pressure–volume diagrams from the modified Soave–Redlich–Kwong (SRK) equations of state with the Soave and exponential type alpha functions for the 90.00 mol.% C₈H₁₈–10.00 mol.% CH₄ mixtures at the temperature of $T = 311.15$ K and pore radius of $r_p = 3.5$ nm.
Figure 3.18b Measured (Cho et al., 2017) and calculated pressure–volume diagrams from the modified Soave–Redlich–Kwong (SRK) equations of state with the Soave and exponential type alpha functions for the 90.00 mol.% C₈H₁₈–10.00 mol.% CH₄ mixtures at the temperature of $T = 311.15$ K and pore radius of $r_p = 3.7$ nm.
Figure 3.19a Measured (Y. Liu et al., 2018) and calculated pressure–volume diagrams from the modified Soave–Redlich–Kwong (SRK) equations of state with the Soave and exponential type alpha functions for the 5.40 mol.% N₂–94.60 mol.% n-C₄H₁₀ mixtures at pore radius of $r_p = 5.0$ nm and the temperatures of $T = 299.15$ K.
Figure 3.19b Measured (Y. Liu et al., 2018) and calculated pressure–volume diagrams from the modified Soave–Redlich–Kwong (SRK) equations of state with the Soave and exponential type alpha functions for the 5.40 mol.% N₂–94.60 mol.% n-C₄H₁₀ mixtures at pore radius of $r_p = 5.0$ nm and the temperatures of $T = 324.15$ K.
3.5 Summary

In this chapter, two new nanoscale-extended alpha functions in Soave and exponential types (i.e., M-Soave and M-exponential) are developed analytically by considering a series of confinement effects for the first time, which are applied and evaluated for calculating the thermodynamic and phase properties of confined fluids coupled with a modified SRK EOS.

The developed alpha functions have been validated to be accurate for the phase and thermodynamic property calculations in bulk phase and nanopores. The minimum reduced temperature from the Soave alpha function occurs at the acentric factor of \( \omega = -0.295 \), whereas the exponential alpha function has a monotonic relationship with the reduced temperature and no minimum conditions can be determined. Furthermore, a new method is proposed to determine the nanoscale acentric factors. The acentric factors are increased with the pore radius reductions that the acentric factors remain constant or slightly increase with the pore radius reductions at \( r_p \geq 50 \) nm while they become quickly increased once the pore radius is smaller than 50 nm. The Soave alpha functions are related to the temperatures in concave upward parabola curves while the exponential type are monotonically decreased and asymptotically approaching zero with temperature increases. The dimensionless attractive term \( A \) in the two types follow the similar patterns of the alpha functions in nanopores while they decrease monotonically and asymptotically approach zero with temperature increases in bulk phase. The alpha functions and attractive term \( A \) in the both types for different components become more sensitive to the temperature increases with the pore radius reductions to different extent, wherein the significant differences occur at \( r_p < 50 \) nm for the CO\(_2\) and alkanes and at \( r_p < 10 \) nm for the N\(_2\). Moreover, the
intermolecular attractivities are stronger for the heavier or high carbon number components. Some abnormal phenomena take place with the pore radius reductions. The Soave alpha functions of the N$_2$ are more sensitive to the temperatures in bulk phase but become more insensitive at $r_p = 10$ nm in comparison with the CO$_2$ case. It is also found that the alpha functions are decreased with the pore radius reductions at the critical temperature ($T_r = 1$), which are opposite to the cases at other temperatures.

The first and second derivatives of the Soave and exponential alpha functions to the temperatures are continuous at $T \leq 4000$ K. The reason to do the calculations up to 4000 K, which may not be common in the reality, is purely to present the general calculation trend of the target functions. The first derivatives in the two types are always increased while the second derivatives are reduced with the temperature increases to different extent in bulk phase and nanopores, all of which become more sensitive to the temperatures at smaller pore radii. The original and nanoscale-extended alpha functions in Soave and exponential types have been validated to be accurate in bulk phase and nanopores. Some of them may be slightly better for some case calculations but none of them can be a general alpha function which always performs the best for all case calculations.
CHAPTER 4  INTERFACIAL TENSION DETERMINATIONS AND EVALUATIONS

At the liquid–liquid/gas interfaces, the adjacent layers with dissimilar molecules are in the force fields, which are much different from those in the bulk fluid phase (S. Zhang et al., 2018). The layers are always considered to be relatively separate phases due to their distinctive physicochemical properties, such as different intermolecular distances, pressures, or chemical potentials (Fathinasab et al., 2018; Lashkarbolooki and Ayatollahi, 2018). Thus, there are two distinct interfacial monolayers existing at a liquid–liquid interface and each of them has a tension (or pressure) different from that of the bulk liquid phase (Czarnota et al., 2018). By convention, the interfacial tension (IFT) of the liquid–liquid system is the summation of the tensions for these two monolayers (Cumicheo et al., 2018). By definition, the IFT is the amount of work required to bring the molecules from the bulk phases to the contact interface of unit area (Ameli et al., 2018; Hemmati-Sarapardeh and Mohagheghian, 2017). As an excellent quantitative indicator of the complex interfacial interactions, the IFT can be measured by several experimental methods, such as the axisymmetric drop shape analysis (ADSA) for the pendant and sessile drop cases (Atefi et al., 2014; Zhang and Gu, 2016b) and the spinning drop method (Cayias et al., 1975). Alternatively, they can be predicted by using, for instance, the parachor model (Gharagheizi et al., 2011; Zuo and Stenby, 1997) and linear gradient theory (Enders and Quitzsch, 1998; Li et al., 2008). On the other hand, the importance of the IFT can be exemplified through its influence on many industrial processes, such as chemical reactions (Seo et al., 2018), biological membrane operations (Morris and Homann, 2001), and in particular, oil and gas productions (He et al., 2015; Janiga et al., 2018, 2017). Although the
numerous experimental and theoretical methods have been proposed in bulk phase
aforementioned, few available and applicable method exists for the nanoscale IFT
determinations.

In this chapter, two major parts are included for the IFT determinations and evaluations
in bulk phase and nanopores. Part I: the equilibrium two-phase compositions are predicted
and analyzed to elucidate the pressure dependence of the IFTs of three different light crude
oil–CO$_2$ systems in bulk phase. Part II: a new model based on a generalized equation of
state (EOS) coupled with the parachor model is developed to calculate the IFTs and the
following four important factors are specifically studied to evaluate their effects on the
IFTs in nanopores: feed gas to liquid ratio (FGLR), temperature, pore radius, and wall-
effect distance.

4.1 Pressure-Dependence IFTs in Bulk Phase

4.1.1 Introduction

Over the past several decades, CO$_2$ flooding has been proven to be an effective
enhanced oil recovery (EOR) method and applied to exploit many light and medium oil
reservoirs (Ahmadi et al., 2015; Jarrel et al., 2002). It is worthwhile to emphasize that the
CO$_2$-EOR process not only effectively enhances oil recovery but also considerably reduces
greenhouse gas emissions (Li et al., 2016). The CO$_2$-EOR is largely affected by the
interfacial interactions among the injected CO$_2$, reservoir oil, brine, and rocks (Yang et al.,
2015).

The IFT strongly depends on the pressure and temperature and initial overall fluid
compositions, such as the initial compositions of the oil and gas phases as well as the initial
gas/oil fraction (Ghorbani et al., 2014; Hemmati-Sarapardeh et al., 2013). The IFT between
the equilibrated crude oil and CO$_2$ is an important interfacial property, which is a result of two-way mass transfer: CO$_2$ dissolution into the crude oil and hydrocarbons (HCs)-extraction by CO$_2$ (Zhang et al., 2017b). Therefore, it is important to study the two-way mass transfer between the crude oil and CO$_2$ and analyze the IFTs under the actual oil reservoir conditions. In the literature, the IFT is found to reduce almost linearly with test pressure in two or three distinct pressure ranges (Wang et al., 2010). The IFT in a relatively low test pressure range is quickly decreased with the test pressure until a sudden slope change occurs. The quick IFT reduction in the first pressure range was mainly attributed to quick CO$_2$ dissolution into the crude oil (Naseri et al., 2015). Afterward, the IFT reduction tends to be gradual in the second or third pressure range.

On the other hand, the initial overall fluid compositions, i.e., the initial oil and gas compositions as well as the initial gas fraction, are considered to have the foremost and dominant effect on the IFT (Ayirala and Rao, 2011; Zhang et al., 2017a; Zhang and Gu, 2015). For example, the live light crude oil–CO$_2$ system pre-saturated with CH$_4$-dominated HCs was found to have a higher IFT (Gu et al., 2013), whereas a lower IFT was measured between the intermediate HCs pre-saturated oil and CO$_2$ phase (Escrochi et al., 2013). In addition, the initial gas (e.g., CO$_2$) fraction effect on the IFT cannot be ignored, though there is still no general consensus on it. In some early studies, the initial CO$_2$ fraction was considered to affect how quickly to achieve the equilibrium state but have no effect on the IFT (Ayirala and Rao, 2011). Later, it was found that the IFT reached a minimum value when the initial gas–oil ratio (GOR) was equal to 1:1 sm$^3$/sm$^3$ but was slightly increased at an increased initial GOR (Zhang and Gu, 2015).

In the literature, two terminologies, the miscibility and saturation, are commonly used
in phase behaviour studies of the light crude oil–CO₂ systems (Ayirala and Rao, 2006). It was stated that the zero IFT is a necessary and sufficient condition for the miscibility to be achieved (Rao, 1997). If the test pressure is at or above the saturation pressure of the light crude oil–CO₂ system, zero IFT can be obtained when the two phases become one phase at the saturation conditions (Whitson and Brule, 2000). Physically, zero IFT is achieved once the miscibility or saturation is reached. Further studies are needed to clearly distinguish the two different zero-IFT cases under the miscible and saturation conditions, respectively. In this part, three respective series of the IFT tests for three different light crude oil–pure/impure CO₂ systems at different equilibrium pressures and \(T_{res} = 53.0°C\) are used from the literature (Gu et al., 2013; Zhang and Gu, 2015). Then, a commercial simulation module is applied to model the phase behaviour of the three light crude oil–CO₂ systems. An EOS and the parachor model are used to predict the equilibrium two-phase compositions and IFTs, respectively. Furthermore, the predicted equilibrium two-phase compositions are used to analyze the pressure dependence of the IFTs, the initial oil and gas composition effects, as well as the initial gas fraction effect on the predicted IFTs.

4.1.2 Experimental section

Materials

In this previous study (Zhang, 2016), a dead light crude oil sample of the Pembina oilfield, Cardium formation in Alberta (Canada), was collected. The gas chromatography (GC) compositional analysis of the cleaned light crude oil was performed and the detailed result can be found elsewhere (Zhang, 2016). Purities of pure carbon dioxide (CO₂) and \(n\)-pentane were equal to 99.998 and 99.76 mol.%, which were purchased from Praxair (Canada) and VWR International (Canada), respectively. In addition, a live oil sample and
an impure CO\textsubscript{2} sample were prepared (Zhang and Gu, 2016a, 2016b). The live oil with a GOR of 15:1 sm\textsuperscript{3}/sm\textsuperscript{3} was reconstituted by saturating the dead crude oil sample with the produced HC gas. The actual composition of the produced gas was equal to 66.50 mol.% CH\textsubscript{4} + 11.41 mol.% C\textsubscript{2}H\textsubscript{6} + 11.39 mol.% C\textsubscript{3}H\textsubscript{8} + 10.70 mol.% n-C\textsubscript{4}H\textsubscript{10}. On the other hand, pure CO\textsubscript{2} and pure CH\textsubscript{4} were mixed to reach a pre-specified composition of 75 mol.% CO\textsubscript{2} + 25 mol.% CH\textsubscript{4} so that the impure CO\textsubscript{2} sample was prepared. The detailed experimental setups and procedures for preparing the live oil sample and the impure CO\textsubscript{2} sample were described elsewhere (Zhang, 2016). The detailed compositions of the Pembina dead and live light crude oils as well as two different solvents (i.e., pure and impure CO\textsubscript{2} samples) used are summarized and listed in Table 4.1.

**PVT studies**

A mercury-free pressure–volume–temperature (PVT) system (PVT-0150-100-200-316-155, DBR, Canada) was used to measure the PVT data of the dead light crude oil–CO\textsubscript{2} system with four different CO\textsubscript{2} concentrations at $T_{\text{res}} = 53.0^\circ\text{C}$ (Zhang, 2016). The experimental setup and procedure of the PVT tests were described previously. It is found that the experimentally measured saturation pressure, oil density, and oil-swelling factor (SF) increase with CO\textsubscript{2} concentration due to the CO\textsubscript{2} dissolution. It is worthwhile to mention that the density of light liquid hydrocarbon (e.g., light crude oil) is increased with more CO\textsubscript{2} dissolutions, the detailed technical explanations of which can be found in the previous studies (Ashcroft and Isa, 1997; Farajzadeh et al., 2009). As described at a later time, in this work, the measured PVT data were used to tune the modified Peng–Robinson EOS.
Table 4.1
Compositions of the Pembina dead and live light crude oils as well as two different solvents (i.e., pure and impure CO₂ samples) used in this study.

<table>
<thead>
<tr>
<th>Component</th>
<th>Pembina dead oil Composition (mol.%)</th>
<th>Pembina live oil composition (mol.%)</th>
<th>Solvent</th>
<th>Solvent I (mol.%)</th>
<th>Solvent II (mol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>0.00</td>
<td>62.35</td>
<td>CO₂</td>
<td>100.00</td>
<td>75.00</td>
</tr>
<tr>
<td>C₂</td>
<td>0.00</td>
<td>10.70</td>
<td>C₁</td>
<td>0.00</td>
<td>25.00</td>
</tr>
<tr>
<td>C₃</td>
<td>0.20</td>
<td>10.69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₄</td>
<td>1.17</td>
<td>10.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅–₆</td>
<td>8.68</td>
<td>0.54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₇–₁₂</td>
<td>43.19</td>
<td>2.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₃–₂₉</td>
<td>36.77</td>
<td>2.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃₀+</td>
<td>9.99</td>
<td>0.62</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
IFT tests

The equilibrium IFTs between the light crude oil and CO$_2$ are measured by applying the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case, which was described in detail elsewhere (Zhang, 2016; Zhang and Gu, 2016b). The pressure and temperature rating of a high-pressure IFT cell (IFT-10, Temco, USA) are equal to $P_{\text{max}} = 69.0$ MPa and $T_{\text{max}} = 177.0^\circ$C. The IFT-cell volume was measured to be $V_{\text{cell}} = 49.5$ cm$^3$. The ADSA program requires the density difference between the oil drop and the CO$_2$ phase at the test conditions and the local gravitational acceleration as the input data. The dead/live oil sample densities at different test conditions were measured experimentally by using a densitometer (DMA512P, Anton Paar, USA) (Zhang and Gu, 2016a). The CO$_2$ density was predicted by using the CMG WinProp module (Version 2016.10, Computer Modelling Group Limited, Canada) under the same test conditions, which are also verified by comparing with the recorded data from the National Institute of Standards and Technology.

Three respective series of the dynamic IFT tests for the dead light crude oil–pure CO$_2$ system, live light crude oil–pure CO$_2$ system, and dead light crude oil–impure CO$_2$ system were conducted at $T_{\text{res}} = 53.0^\circ$C (Zhang, 2016). The detailed experimental data of these three series of the IFT tests are listed in Table 4.2.

4.1.3 EOS modeling

In the EOS modeling, a crude oil is often represented by several pseudo-components with different lumping/splitting schemes. Given the oil compositional analysis result, in this work, the modified Peng–Robinson EOS (PR-EOS, 1978) (Haghtalab et al., 2011) in the CMG WinProp module was applied to study the phase behaviors of the dead light crude
Table 4.2

Measured and calculated equilibrium interfacial tensions (IFTs) at different pressures and $T_{\text{res}} = 53.0^\circ\text{C}$ for the dead light crude oil–pure CO$_2$ system, live light crude oil–pure CO$_2$ system, and dead light crude oil–impure CO$_2$ system, respectively (Zhang, 2016).

<table>
<thead>
<tr>
<th>Dead light crude oil–pure CO$_2$ system</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{eq}}$ (MPa)</td>
<td>2.0</td>
</tr>
<tr>
<td>$\gamma_{\text{eq}}^m$ (mJ/m$^2$)</td>
<td>16.89</td>
</tr>
<tr>
<td>$\gamma_{\text{eq}}^c$ (mJ/m$^2$)</td>
<td>16.54</td>
</tr>
<tr>
<td>AD (%)</td>
<td>2.07</td>
</tr>
</tbody>
</table>

| Live light crude oil–pure CO$_2$ system |
|---|---|
| $P_{\text{eq}}$ (MPa) | 1.8 | 3.0 | 3.8 | 4.8 | 5.6 | 7.0 | 8.6 | 10.1 | 11.4 | 15.0 | 16.6 | 18.1 |
| $\gamma_{\text{eq}}^m$ (mJ/m$^2$) | 17.77 | 15.24 | 13.79 | 12.67 | 10.81 | 8.75 | 5.89 | 4.34 | 4.04 | 3.28 | 2.56 | 1.75 |
| $\gamma_{\text{eq}}^c$ (mJ/m$^2$) | 17.13 | 15.19 | 13.91 | 12.31 | 11.01 | 8.75 | 6.17 | 4.12 | 2.93 | 2.02 | 1.52 | 1.03 |
| AD (%) | 3.60 | 0.33 | 0.87 | 2.84 | 1.85 | 0.00 | 4.75 | 5.07 | 27.48 | 38.41 | 40.63 | 41.14 |

| Dead light crude oil–impure CO$_2$ system |
|---|---|
| $P_{\text{eq}}$ (MPa) | 2.0 | 3.0 | 4.5 | 6.0 | 7.0 | 8.5 | 10.0 | 12.5 | 15.0 | 19.0 | 21.0 | 24.0 |
| $\gamma_{\text{eq}}^m$ (mJ/m$^2$) | 17.56 | 15.99 | 13.93 | 11.58 | 9.69 | 7.82 | 5.95 | 4.11 | 3.01 | 2.05 | 1.88 | 1.34 |
| $\gamma_{\text{eq}}^c$ (mJ/m$^2$) | 16.74 | 15.38 | 13.01 | 10.84 | 9.44 | 7.45 | 5.74 | 3.16 | 2.28 | 1.43 | 1.12 | 0.93 |
| AD (%) | 4.90 | 3.97 | 7.07 | 6.83 | 2.65 | 4.97 | 3.66 | 30.06 | 32.02 | 43.36 | 67.86 | 44.09 |

Notes: $m$: measured equilibrium IFTs  
c: calculated equilibrium IFTs
oil–pure CO₂ system at different pressures and \( T_{res} = 53.0^\circ C \). Any \( C_{30} \) plus alkanes of the original crude oil were lumped altogether as a plus pseudo-component \( (C_{30}+) \) because the components of \( C_{30}+ \) account for only 9.99 mol.% of the original light crude oil tested in this study. To be consistent with the PVT tests, four different light crude oil–CO₂ mixtures with four different CO₂ concentrations of 0.0, 35.9, 42.7, and 51.7 mol.% were chosen and modeled. Then, three calculation sectors of the saturation pressure, two-phase flash, and swelling test were applied to predict the saturation pressure, oil density, and oil-swelling factor, respectively.

In this study, the modified PR-EOS was first tuned by using a set of major tuning parameters (Agarwal et al., 1987). More specifically, the binary interaction coefficient (BIC) between CO₂ and \( C_{30}+ \), critical pressure and temperature, and acentric factor of \( C_{30}+ \), as well as volume translation parameter were adjusted to match the measured PVT data. Second, the measured PVT data were used together with a multi-variable regression scheme available in the CMG WinProp module, where the upper and lower limits of the five tuning parameters were adjusted until the differences between the predicted and measured PVT data become sufficiently small.

### 4.1.4 Parachor model

The parachor model is most commonly used by the petroleum industry to predict the equilibrium IFT of an oil–gas system (Zuo and Stenby, 1997). Macleod (Macleod, 1923) first related the surface tension between the liquid and vapour phases of a pure component to its parachor and the molar density difference between the two phases,

\[
\sigma = [p(\rho_L - \rho_V)]^4
\]  

(4.1)

where \( \sigma \) is the equilibrium surface tension in mJ/m²; \( p \) is the parachor.
At a later time, Eq. (4.1) was extended to a multi-component mixture (Weinaug and Katz, 1943),

$$\gamma_{eq} = (\rho_1 \sum_{i=1}^{r} x_i p_i - \rho_v \sum_{i=1}^{r} y_i p_i)^4$$  \hspace{1cm} (4.2)$$

where $\gamma_{eq}$ is the equilibrium IFT between the vapour and liquid bulk phases of the multi-component mixture; $x_i$ and $y_i$ are the respective mole percentages of the $i^{th}$ component in the liquid and vapour bulk phases, $i = 1, 2, \ldots, r$; $r$ is the component number in the mixture; and $p_i$ is the parachor of the $i^{th}$ component.

In this study, the liquid and vapour phases are referred to as the oil and gas phases, respectively. Since $\rho_o = \frac{m_o}{V_o}$ and $\rho_g = \frac{P MW_g}{Z_g RT}$, Eq. (4.2) is rewritten as,

$$\gamma_{eq} = \left( \frac{m_o}{V_o} \sum_{i=1}^{r} x_i p_i - \frac{P MW_g}{Z_g RT} \sum_{i=1}^{r} y_i p_i \right)^4$$ \hspace{1cm} (4.3)$$

where $m_o$ is the oil phase mass in kg; $V_o$ is the oil phase volume in m$^3$; $P$ is the pressure in Pa; $MW_g$ is the molecular weight of the gas phase in kg/kmol.; $Z_g$ is the gas phase compressibility factor; $R$ is the universal gas constant in JK$^{-1}$mol$^{-1}$; $T$ is the temperature K.

The parachor model together with the tuned PR-EOS is used to predict the equilibrium IFTs of the three light crude oil–CO$_2$ systems at twelve different pressures and $T_{res} = 53.0^\circ$C. The predicted equilibrium IFTs of the three respective light crude oil–CO$_2$ systems are summarized and compared with the measured equilibrium IFTs in Table 4.2.

### 4.1.5 Results and discussion

**Measured and predicted equilibrium IFTs**

In this part, the measured (Zhang, 2016) and predicted equilibrium IFTs are plotted in
Figures 4.1a–c for the dead light crude oil–pure CO₂ system, live light crude oil–pure CO₂ system, and dead light crude oil–impure CO₂ system at different equilibrium pressures and $T_{res} = 53.0^\circ C$, respectively. It is found by trial and error that the predicted IFTs at the initial gas mole fraction of 0.90 agree well with the measured IFTs. From Table 4.2 and Figures 4.1a–c, the measured and predicted equilibrium IFTs match well especially at lower pressures, both of which are quickly reduced with the pressure. When the pressure is higher than 10 MPa, the predicted IFT is lower than the measured IFT. In the IFT tests, the pendant oil drop that was formed eventually is mainly consisted of relatively heavy paraffinic (i.e., HCs), aromatic, or asphalnic components of the original dead light crude oil after the initial quick and subsequent slow HCs-extractions by CO₂ at a higher pressure (Yang and Gu, 2005). Thus the measured IFT at a higher pressure is between the remaining oil phase and the CO₂ phase with some extracted light to intermediate HCs. In the EOS modeling, however, the light crude oil is characterized and represented by using a series of alkanes (i.e., $C_3$–$C_{30}$+) rather than a combination of the paraffinic, aromatic, or asphalnic molecules. The predicted IFT is between the intermediate to heavy alkanes of the light crude oil and the CO₂ phase with some extracted light to intermediate alkanes at a higher pressure. This is why the predicted IFT is lower than the measured IFT at a higher pressure.

Figures 4.1a and b show that at a relatively higher pressure, the measured IFT of the live light crude oil–pure CO₂ system is reduced more slowly than that of the dead oil–pure CO₂ system. There might be some asphaltene precipitation in the former system.
Figure 4.1a Measured (Zhang, 2016) and predicted equilibrium interfacial tensions (IFTs) of the dead light crude oil–pure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{res} = 53.0^\circ$C.
Figure 4.1b Measured (Zhang, 2016) and predicted equilibrium interfacial tensions (IFTs) of the live light crude oil–pure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{res}$ = 53.0°C.
Figure 4.1c Measured (Zhang, 2016) and predicted equilibrium interfacial tensions (IFTs) of the dead light crude oil–impure CO₂ system at the initial gas mole fraction of 0.90 and $T_{\text{res}} = 53.0^\circ\text{C}$. 
In the live light crude oil–pure CO₂ system, the added light HCs (i.e., C₂H₆, C₃H₈, and n-C₄H₁₀) are rather different from resins and asphaltenes in terms of the molecular weight, size, and structure. This fact leads to the possible desorption of resins from the surfaces of the dispersed asphaltenes and causes more asphaltenes to precipitate (Kazemzadeh et al., 2015). Therefore, the measured IFTs of the live light crude oil–pure CO₂ system at relatively higher pressures are reduced more slowly than those of the dead light crude oil–pure CO₂ system.

**Equilibrium two-phase compositions**

It is well known that the equilibrium IFT is an important interfacial property between the equilibrated crude oil and gas phases as a result of the two-way mass transfer (Zhang et al., 2018e). Hence, it is necessary to study the two-way mass transfer in order to better analyze and understand the pressure dependence of the equilibrium IFTs of a given light crude oil–CO₂ system. Figures 4.2a–c show \( x_{\text{CO}_2}, y_{\text{HCs}}, \) and \( x_{\text{CO}_2} + y_{\text{HCs}} \) vs. pressure data of the above-mentioned three light crude oil–CO₂ systems at \( T_{\text{res}} = 53.0°C \). Here, \( x_{\text{CO}_2} \) stands for pure/impure CO₂ mole fraction in the liquid (oil) phase due to solvent dissolution and \( y_{\text{HCs}} \) denotes the extracted HCs mole fraction in the gas phase. Physically, \( x_{\text{CO}_2} + y_{\text{HCs}} \) represents the overall or total compositional change that is attributed to the two-way mass transfer. In this study, \( x_{\text{CO}_2} + y_{\text{HCs}} \) is referred to as the two-way mass transfer index (MTI) for brevity, which changes in the range of 0 to 1. The MTI is equal to zero if the two phases are completely insoluble. It is equal to unity if the two phases are miscible or if one phase (gas) is completely dissolved into the other phase (liquid), i.e., the complete dissolution.
Figure 4.2a Predicted $x_{\text{CO}_2}$, $y_{\text{HCs}}$, and $x_{\text{CO}_2} + y_{\text{HCs}}$ of the dead light crude oil–pure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{\text{res}} = 53.0^\circ \text{C}$. 
Figure 4.2b Predicted $x_{CO_2}$, $y_{HC_s}$, and $x_{CO_2} + y_{HC_s}$ of the live light crude oil–pure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{res} = 53.0^\circ$C.
Figure 4.2c Predicted $x_{CO_2}$, $y_{HC_s}$, and $x_{CO_2} + y_{HC_s}$ of the dead light crude oil–impure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{res} = 53.0^\circ$C.
It is found from Figures 4.2a–c that $x_{CO_2}$ is quickly increased with the pressure up to a certain pressure threshold, above which $x_{CO_2}$ is increased gradually and finally reaches its maximum. The gaseous CO$_2$ is much more easily dissolved into the oil phase than the liquid CO$_2$ (Chen et al., 2013). On the other hand, $y_{HCs}$ is slightly decreased at a lower pressure, which is followed by an obvious increase starting from the pressure threshold, at which a strong HCs-extraction occurs because the liquid CO$_2$ has a stronger extraction ability than the gaseous CO$_2$. At an even higher equilibrium pressure, $y_{HCs}$ increases much more gradually because most light to intermediate HCs in the crude oil phase have already been extracted.

In addition, the two-way MTI ($x_{CO_2} + y_{HCs}$) has a similar trend to $x_{CO_2}$ because $x_{CO_2}$ represents over 90% of the total compositional change and becomes a dominant component in the liquid phase at a high pressure. Hence, three equilibrium pressure ranges can be defined and determined in terms of the two-way MTI by using two dividing or threshold equilibrium pressures, $P^A_{eq}$ and $P^B_{eq}$, which are marked in Figures 4.2a–c. It is found from Eq. (4.3) that the predicted IFT from the parachor model largely depends on the molecular weight ($MW_g$) and compressibility ($Z_g$) of the gas phase. Figure 4.3 shows the forward finite difference approximation of the partial derivative, $\partial(MW_g / Z_g) / \partial P_{eq}$, for the each light crude oil–CO$_2$ system. Three respective threshold pressures of $P^A_{eq} = 10.8, 11.3,$ and $13.5$ MPa are determined for the three light crude oil–CO$_2$ systems and marked in Figure 4.3, where each partial derivative reaches its maximum. Since $y_{HCs}$ is sufficiently small at $P_{eq} \leq P^A_{eq}$, $x_{CO_2} + y_{HCs}$ also reaches its maximum at $P^A_{eq}$ because quick CO$_2$ dissolution is
Figure 4.3 Calculated forward finite difference approximation of the partial derivative
\[
\frac{\partial (MW_g/Z_g)}{\partial P_{eq}}
\] for the dead light crude oil–pure CO\textsubscript{2} system with \(P_{eq}^\Lambda = 10.8\) MPa, the live light crude oil–pure CO\textsubscript{2} system with \(P_{eq}^\Lambda = 11.3\) MPa, and the dead light crude oil–impure CO\textsubscript{2} system with \(P_{eq}^\Lambda = 13.5\) MPa at the initial gas mole fraction of 0.90 and \(T_{res} = 53.0^{\circ}\text{C}\).
completed. The pressure dependence of the equilibrium IFT up to $P_{eq} = P_{eq}^A$ is a result of quick CO$_2$ dissolution. Therefore, $P_{eq}^A$ marked for each light crude oil–CO$_2$ system in each of Figure 4.3 corresponds to the same threshold equilibrium pressure marked in each of Figures 4.2a–c.

On the other hand, the incremental two-way MTI $x_{CO_2} + y_{HCs}$ change per incremental pressure is reduced to and remains under 1 mol.%/MPa at an even higher threshold equilibrium pressure ($P_{eq} = P_{eq}^B$), above which the two-way MTI remains almost the same and the two-way mass transfer is almost completed. In this study, three respective threshold equilibrium pressures of $P_{eq}^B = 13, 15, \text{ and } 23 \text{ MPa}$ are determined by using the 1 mol.%/MPa criterion of the two-way MTI change for the three light crude oil–CO$_2$ systems and marked in Figures 4.2a–c, respectively.

**Equilibrium fluid densities and IFTs**

In the experiment, the ADSA program requires the density difference between the crude oil and gas phases as an input datum for measuring the equilibrium IFT. In theory, the densities of the crude oil and gas phases are the important parameters in the parachor model for predicting the equilibrium IFT. In this study, the densities of the light crude oil and gas phases as well as their differences $(\rho_o - \rho_g)^4$ for the three light crude oil–CO$_2$ systems are predicted and plotted in Figures 4.4a–c. It is found that as the equilibrium pressure is increased, the oil density is slightly increased in the dead or live light crude oil–pure CO$_2$ system, whereas it is slightly decreased in the dead oil–impure CO$_2$ system. The light crude oil becomes heavier due to pure CO$_2$ dissolution but lighter because of dissolution of the impure CO$_2$ with some CH$_4$. In contrast to the oil density, the gas density of each light
Figure 4.4a Predicted densities of the oil ($\rho_o$) and gas ($\rho_g$) phases as well as their differences ($\rho_o - \rho_g$) for the dead light crude oil–pure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{res} = 53.0^\circ$C.
Figure 4.4b Predicted densities of the oil ($\rho_o$) and gas ($\rho_g$) phases as well as their differences ($\rho_o - \rho_g$) for the live light crude oil–pure CO2 system at the initial gas mole fraction of 0.90 and $T_{res} = 53.0^\circ$C.
Figure 4.4c Predicted densities of the oil ($\rho_o$) and gas ($\rho_g$) phases as well as their differences $(\rho_o - \rho_g)^4$ for the dead light crude oil–impure CO$_2$ system at the initial gas mole fraction of 0.90 and $T_{res} = 53.0^\circ$C.
crude oil–CO\(_2\) system is drastically increased with the equilibrium pressure in three different ranges. At a low pressure, the gas density is proportionally increased with the equilibrium pressure mainly due to gas compression. Then there is a more quick gas density increase because of strong HCs-extraction. Lastly, the gas density increases gradually because the HCs-extraction is near its completion. Thus the reduction of the density difference between the oil and gas phases is mainly attributed to the two-way mass transfer. Furthermore, the two-phase density differences \((\rho_o - \rho_g)^4\) for the three light crude oil–CO\(_2\) systems are required in the parachor model and also plotted in Figures 4.4a–c, which match well with the equilibrium IFT vs. pressure curves in Figures 4.5a–c. Hence, the density difference between the oil and gas phases is a key factor in the parachor model for predicting the equilibrium IFTs.

Physically, the two-phase density changes are related to the equilibrium two-phase compositions. Accordingly, each equilibrium IFT vs. pressure curve in Figures 4.1a–c also has three different pressure ranges. The equilibrium two-phase compositions determine the density difference vs. pressure curve in each pressure range. The IFT reduction between the crude oil and gas phases is mainly attributed to the reduction of their density difference. In this study, it is found that the IFT reductions in the three pressure ranges are caused by the initial gas dissolution and compression as well as light-HCs vapourization, the subsequent strong HCs-extraction, and the final weak HCs-extraction, respectively. Therefore, the slope change of the equilibrium IFT vs. pressure curve depends on the density changes of the crude oil and gas phases, which are related to the equilibrium two-phase compositions.
Figure 4.5a Predicted equilibrium interfacial tensions ($\gamma_{eq}$) of the dead light crude oil–pure CO$_2$ system at seven different initial gas mole fractions of 0.01–0.99 and $T_{res} = 53.0^\circ$C.
Figure 4.5b Predicted equilibrium interfacial tensions ($\gamma_{eq}$) of the live light crude oil–pure CO$_2$ system at seven different initial gas mole fractions of 0.01–0.99 and $T_{res} = 53.0^\circ$C.
Figure 4.5c Predicted equilibrium interfacial tensions ($\gamma_{eq}$) of the dead light crude oil system at seven different initial gas mole fractions of 0.01–0.99 and $T_{res} = 53.0^\circ$C.
**Initial oil and gas composition effects**

The initial oil and gas compositions affect both CO\textsubscript{2} dissolution into the oil phase and HCs-extraction by CO\textsubscript{2} phase, which determine the equilibrium IFTs. It can be seen from Figures 4.2a–c that \(x_{\text{CO}_2}\) and \(y_{\text{HCS}}\) of the three light crude oil–CO\textsubscript{2} systems are rather different due to different initial oil and gas compositions. More specifically, \(x_{\text{CO}_2}\) of the live light crude oil–pure CO\textsubscript{2} system in Figure 4.2b is relatively lower, whereas its \(y_{\text{HCS}}\) is significantly higher than those of the dead light crude oil–pure and impure CO\textsubscript{2} systems. The live oil sample was reconstituted by adding some CH\textsubscript{4}-dominated light HCs into the original dead oil. Thus the solubility of CO\textsubscript{2} in the live oil is much reduced with the presence of CH\textsubscript{4} in the oil phase because CO\textsubscript{2} is forced to interact with and displace CH\textsubscript{4} before it is dissolved into the oil phase (Chen et al., 2013). On the other hand, these added light HCs are vaporized quickly to become the gas phase. This is why the live light crude oil–pure CO\textsubscript{2} system has a relatively lower \(x_{\text{CO}_2}\) but a much higher \(y_{\text{HCS}}\), which lead to its higher equilibrium IFT than that of the dead light crude oil–pure CO\textsubscript{2} system.

In this study, the initial gas composition effect is purposely studied by adding approximately 25 mol.% CH\textsubscript{4} into pure CO\textsubscript{2} to prepare the impure CO\textsubscript{2} phase. In practice, the injected pure CO\textsubscript{2} will be likely co-produced with some solution gases and re-injected in a field-scale CO\textsubscript{2}-EOR project (Ahmadi et al., 2015). Either \(x_{\text{CO}_2}\) or \(y_{\text{HCS}}\) of the dead oil–impure CO\textsubscript{2} system in Figure 4.2c is increased more slowly with the pressure in comparison with that of the dead light crude oil–pure CO\textsubscript{2} system in Figure 4.2a. Obviously, CH\textsubscript{4} has a rather lower solubility in the oil phase and a much weaker ability to extract the other light or intermediate HCs from the oil phase to the gas phase. Thus, the presence of
CH₄ in the gas phase is found to hinder the two-way mass transfer. This is why at the same pressure, the dead oil–impure CO₂ (CH₄ + CO₂) equilibrium IFT is much higher than that of the dead light crude oil–pure CO₂ system.

It is also seen from Figures 4.1a–c that a higher pressure is required to reduce the IFT for either the live oil–pure CO₂ system or the dead oil–impure CO₂ system. However, the IFT is found to be more sensitive to the initial gas composition than to the initial oil composition. This is because the equilibrium IFT is dependent on the density difference between the crude oil and gas phases to a large extent. The gas density change is much larger than the oil density change. In this study, Figures 4.4a–c show that the density difference between the light crude oil and gas phases is mainly determined by the gas density since the oil density change is small for each light crude oil–CO₂ system. Hence, the initial gas composition has a stronger effect on the equilibrium IFT than the initial oil composition.

**Initial gas fraction effect**

Figures 4.5a–c show the predicted equilibrium IFTs of the dead and live oil–pure and impure CO₂ systems at seven different initial gas mole fractions of 0.01–0.99 and T<sub>res</sub> = 53.0°C. The initial gas fraction effect on the equilibrium IFT is found to be weak in Figure 4.5a or c so that the equilibrium IFTs of the dead light crude oil–pure or impure CO₂ system are almost the same at different initial gas fractions. Figures 4.5a and c also show that the equilibrium IFTs at the initial gas mole fractions of ≤ 0.70 are always suddenly reduced to and remain at zero at the pressure is above the saturation pressure when the oil and gas phases become one phase. Figure 4.5b shows that the equilibrium IFT of the live oil–pure
CO₂ system at a low initial gas fraction is lower at a lower equilibrium pressure but it becomes higher at a higher equilibrium pressure. The above-mentioned two findings can be explained by using the two-way MTI indexes at different initial gas fractions. Figures 4.6a–c show the two-way MTIs \( (x_{\text{CO}_2} + y_{\text{HC}_a}) \) of the three light crude oil–CO₂ systems at the initial gas mole fractions of 0.01–0.99. It is seen from Figures 4.6a and c that the two-way MTIs of the dead light crude oil–pure and impure CO₂ systems are similar at different initial gas fractions. Nevertheless, the two-way MTI of the live light crude oil–pure CO₂ system at the same pressure is higher at a lower initial gas fraction, as shown in Figure 4.6b.

In addition, the two-way MTI is also used to study the initial gas fraction effect on the miscibility by using the aforementioned 1 mol.%/MPa criterion. Precisely speaking, the miscibility is considered to be achieved when zero-IFT case occurs and the incremental two-way MTI change per incremental pressure is less than 1 mol.%/MPa. Otherwise, a sudden reduction to zero IFT in Figures 4.5a–c or a sudden increase of the two-way MTI from a relatively lower value to the unity in Figures 4.6a–c is attributed to the complete CO₂ dissolution rather than CO₂ miscibility. Physically, the two-way MTI represents the overall or total compositional change between the two phases and should reach its maximum at some threshold pressure if the miscibility between the two phases is achieved. Hence, the miscibility of the dead light crude oil–pure or impure CO₂ system can be achieved only when the initial gas mole fraction is higher than 0.70 at \( T_{\text{res}} = 53.0^\circ\text{C} \). Otherwise, it is the complete pure or impure CO₂ dissolution into the light crude oil that leads to zero IFTs in either system at the initial gas mole fractions of \( \leq 0.70 \).
Figure 4.6a Predicted two-way mass transfer indexes \((x_{CO_2} + y_{HCs})\) of the dead light crude oil–pure CO\(_2\) system at seven different initial gas mole fractions of 0.01–0.99 and \(T_{res} = 53.0^\circ C\).
Figure 4.6b Predicted two-way mass transfer indexes \( (x_{CO_2} + y_{HCs}) \) of the live light crude oil–pure CO_2 system at seven different initial gas mole fractions of 0.01–0.99 and \( T_{res} = 53.0^\circ C \).
Figure 4.6c Predicted two-way mass transfer indexes \((x_{\text{CO}_2} + y_{\text{HC}s})\) of the dead light crude oil–impure CO\(_2\) system at seven different initial gas mole fractions of 0.01–0.99 and \(T_{\text{res}} = 53.0^\circ\text{C}\).
4.2 IFT Calculations and Evaluations in Nanopores

4.2.1 Introduction

A number of theoretical models (Ameli et al., 2018; Cho, 2013), numerical simulations (Jayaprakash and Sen, 2018; Jian et al., 2018), and experimental methods (Kuang et al., 2018; Shang et al., 2018) have been conducted to evaluate several important factors and their effects on the IFTs of pure and mixing hydrocarbon (HC) systems in bulk phase. In general, the IFTs are strongly dependent on the temperature, pressure, initial fluid compositions, and feed gas to liquid ratio (FGLR) (Gu et al., 2013; Zhang et al., 2018e; Zhang and Gu, 2016b). In the literature, the pure or mixing HC IFTs are always decreased with the pressure increase at a constant temperature, whereas they are increased by elevating the temperature if the pressure keeps constant (Hemmati-Sarapardeh et al., 2013). The initial fluid compositions are considered to have the foremost and dominant effect on the IFTs from previous studies (Zolghadr et al., 2013). It is found that the IFTs of pure and/or mixing HCs with CO$_2$ systems are substantially increased by adding some lean gas, such as CH$_4$, N$_2$, into the either liquid or gas phase (Gu et al., 2013; Zhang et al., 2017b). Meanwhile, some additions of the intermediate HCs like C$_2$H$_6$ or C$_3$H$_8$ have significant positive contributions to lower the fluid IFTs. Furthermore, the FGLR effect on the IFTs cannot be ignored even though there is no general consensus on it. Some early studies show that the FGLR only affect how quickly the equilibrium state could be reached but has no effect on the IFT values (Rao and Lee, 2002; Zhang and Gu, 2016b). Later, the IFTs are found to reach a minimum value at the FGLR of 1:1 in volume but slightly increase by increasing the gas fraction (Zhang and Gu, 2016b). In recent years, confined fluids in micro or even nanopores draw remarkable attentions in more and more practical applications.
Although abundant research have been implemented on the fluid IFTs in bulk phase (L. Liu et al., 2018a), the IFTs of confined fluids in micro or nanopores are rarely comprehensively studied. So far only some simply modified equations of state (EOS) and molecular simulations studies have been applied to calculate the IFTs and/or evaluate several influential factors (Dong et al., 2016; Goetz and Lipowsky, 1998; Goujon et al., 2018; Shimizu et al., 2018; Teklu et al., 2014b; Zhang et al., 2018b; Zhang et al., 2017a).

The most common conclusion is that the IFTs is decreased with the reductions of pore radius to different extent. Many other important factors, such as the intermolecular interactions, have not been considered in the existing modified EOS and their effects on the IFTs have never been evaluated in nanopores.

In this part, first, a new generalized EOS, which considers the pore radius effect, intermolecular interactions, and wall effect, is developed in the analytical formulation for calculating the thermodynamic phase behaviour of confined pure and mixing fluids in nanopores. Second, the modified model based on the new generalized EOS and coupled with the parachor model, which is also fully capable of modeling the capillary pressure and shifts of critical properties in addition to the above-mentioned confinement effects, is applied to calculate the IFTs of pure and mixing pure systems in nanopores at different conditions. The calculated IFTs from the new model are compared with and verified by the results in bulk phase from the original Peng–Robinson EOS and the IFTs in nanopores from the previously modified PR EOS (Zhang et al., 2017a). Third, the following four important factors are specifically studied to evaluate their effects on the IFTs in nanopores: FGLR, temperature, pore radius, and wall-effect distance (or square-well width).
4.2.2 Experimental

Four different pure and mixing hydrocarbon systems, CO$_2$–C$_{10}$H$_{22}$, CH$_4$–C$_{10}$H$_{22}$, and mixing HCs A and B–CO$_2$ systems (Teklu et al., 2014b; Zhang et al., 2018d), are applied to be specifically evaluated. The detailed properties, e.g., the gas chromatography (GC) compositional analysis results, of the mixing HC A and B were introduced in the literature (Teklu et al., 2014b; Zhang et al., 2018d). The detailed experimental setups and procedures for preparing the mixing HC samples were also described elsewhere (Zhang and Gu, 2016a). In Table 2.1, the critical properties (i.e., temperature, pressure, and volume), vdW EOS constants, and Lennard–Jones and square-well potential parameters for the various components used or maybe mentioned in the subsequent sections are summarized (Sharma and Sharma, 1977; Whitson and Brule, 2000; Yu and Gao, 2000) and listed.

The pressure–volume–temperature (PVT) tests of the C$_{10}$H$_{22}$–CH$_4$ and C$_8$H$_{18}$–CH$_4$ systems were conducted at $T = 311.15$ and $325.15$ K and the pore radii of $r_p = 3.5$ and 3.7 nm (i.e., silica-based mesoporous materials SBA-15 and SBA-16) (Cho et al., 2017). Moreover, a conventional mercury-free PVT system was used to measure the PVT data of the mixing HC A–CO$_2$ system with four different CO$_2$ concentrations at $T = 53.0^\circ$C in bulk phase (Zhang and Gu, 2015), whose measured data are summarized and listed in Table 4.3. The IFTs between the mixing HC A and CO$_2$ are measured by applying the ADSA technique for the pendant drop case, which was described in detail elsewhere (Zhang and Gu, 2016b). Three respective series of the IFT tests for the mixing HC A–pure and impure CO$_2$ systems were conducted at $T = 53.0^\circ$C, whose detailed experimental data can be found in the previous study (Zhang et al., 2017b).
Table 4.3

Measured and calculated saturation pressures, liquid densities, and liquid-swelling factors (SFs) of the mixing hydrocarbon A–pure CO₂ systems at the temperature of \( T = 53.0 \degree \text{C} \) (Zhang and Gu, 2015).

<table>
<thead>
<tr>
<th>Test no.</th>
<th>( x_{\text{CO}_2} )</th>
<th>( P_{\text{sat}}^m ) (MPa)</th>
<th>( P_{\text{sat}}^c ) (MPa)</th>
<th>( \varepsilon_p ) (%)</th>
<th>( \rho_{\text{sat}}^m ) (g/cm(^3))</th>
<th>( \rho_{\text{sat}}^c ) (g/cm(^3))</th>
<th>( \varepsilon_{\rho} ) (%)</th>
<th>( SF_{\text{sat}}^m ) at ( P_{\text{sat}} )</th>
<th>( SF_{\text{sat}}^c )</th>
<th>( \varepsilon_{SF} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.8300</td>
<td>0.8311</td>
<td>0.13</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>10.4</td>
<td>35.9</td>
<td>6.50</td>
<td>6.53</td>
<td>0.46</td>
<td>0.8432</td>
<td>0.8435</td>
<td>0.04</td>
<td>1.16</td>
<td>1.17</td>
</tr>
<tr>
<td>3</td>
<td>13.4</td>
<td>42.7</td>
<td>7.80</td>
<td>7.86</td>
<td>0.77</td>
<td>0.8440</td>
<td>0.8452</td>
<td>0.14</td>
<td>1.20</td>
<td>1.21</td>
</tr>
<tr>
<td>4</td>
<td>18.2</td>
<td>51.7</td>
<td>9.60</td>
<td>9.69</td>
<td>0.94</td>
<td>0.8485</td>
<td>0.8497</td>
<td>0.14</td>
<td>1.28</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Notes:
- \( x_{\text{CO}_2} \): weight or mole percentage of CO₂ dissolved into in the mixing hydrocarbon A
- \( P_{\text{sat}}^m \): measured saturation pressure
- \( P_{\text{sat}}^c \): calculated saturation pressure
- \( \rho_{\text{sat}}^m \): measured liquid density
- \( \rho_{\text{sat}}^c \): calculated liquid density
- \( SF_{\text{sat}}^m \): measured liquid-swelling factor
- \( SF_{\text{sat}}^c \): calculated liquid-swelling factor
- \( \varepsilon \): relative error between the calculated and measured data
4.2.3 Theory

Generalized EOS in nanopores

A generalized EOS for the confined fluid in nanopores is obtained, which considers the confinement-induced effects of pore radius, molecule–molecule and molecule–wall interactions. Figure 4.7 shows the schematic diagrams of the nanopore network model, a single nanopore, and the configuration energy in a single nanopore. The canonical partition function from the statistical thermodynamics is shown as follows (Abrams and Prausnitz, 1975),

\[ Q(N,V,T) = \sum_\tau e^{-E_{\tau}(N,V)/kT} = \frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^N Z(N,V,T) \] (4.4)

where \( N \) is the total number of molecules; \( V \) is the total volume; \( T \) is the temperature; \( E \) is the overall energy state; \( k \) is the Boltzmann constant; \( \Lambda \) is the de Broglie wavelength, \( \Lambda = \left( \frac{\hbar^2}{2\pi m kT} \right)^{0.5} \), \( \hbar \) is the Planck’s constant, \( m \) is the molecular mass; \( q_{\text{int}} \) is the internal partition function; \( Z \) is the configuration partition function, which is expressed as,

\[ Z(N,V,T) = \iiint_V e^{-U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)/kT} d\mathbf{r}_1 d\mathbf{r}_2 \ldots d\mathbf{r}_N \] (4.5)

where \( U \) is the potential energy of entire system of \( N \) number of molecules which positions are described by \( \mathbf{r}_i \), \( i = 1,2,\ldots N \), and \( r_i \) is the separation distance between molecules.

Since the configurational energy \( (E^{\text{conf}}) \) is expressed as,

\[ E^{\text{conf}}(N,V,T) = E(N,V,T) - E(N,V,T = \infty) = kT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_{N,V} \] (4.6)
Figure 4.7 Schematic diagrams of the nano-pore network model (Zhang et al., 2015), nanoscale pore system, and configuration energy in nanoscale pores in this study.
So,
\[
\ln Z(N,V,T) - \ln Z(N,V,T = \infty) = \int_{\infty}^{T} \frac{E_{\text{conf}}(N,V,T)}{kT^2} dT
\]
(4.7)

where only the hard-core repulsive forces between molecules \( Z^{HC}(\rho) \) are important when the configuration integral at infinite temperature, \( Z(N,V,T = \infty) = Z^{HC}(\rho) \).

\( Z^{HC}(N,V,T = \infty) = V_f^N \) is defined from the literature (Sandler, 1985), where \( V_f \) is the free volume. Thus, Eq. (4.7) can be rewritten as,
\[
Z(N,V,T) = V_f^N e^{\frac{\int E_{\text{conf}}(N,V,T) dT}{kT^2}}
\]
(4.8)

The free volume \( V_f \) can be expressed by using the following simple expression (Sandler, 1985),
\[
V_f = V - N\beta = V - \frac{N}{\rho_{\text{max}}}
\]
(4.9)

where \( \beta \) is the excluded volume per fluid molecule and \( \rho_{\text{max}} \) is the molecular density of the full-distributed fluid. Eqs. (4.8) and (4.9) are substituted into Eq. (4.4) to be,
\[
Q(N,V,T) = \sum_i e^{-E_i(N,V)/kT} = \frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^N (V - N\beta)^N e^{\frac{\int E_{\text{conf}}(N,V,T) dT}{kT^2}}
\]
(4.10)

It is worthwhile to mention that \( \rho_{\text{max}} \) is function of the ratio of the pore size \( (r_p) \) and fluid molecule size \( (\sigma) \), \( r_p/\sigma \), whose specific formulation is shown below (Sandler, 1985),
\[
\rho_{\text{max}} = \frac{6}{\pi\sigma^3} (1 - \phi)
\]
(4.11)
\[
\phi = c_1 + c_2 e^{c_3(0.5 - r_p/\sigma)} - c_4 e^{c_5(0.5 - r_p/\sigma)}
\]
(4.12)

where \( \phi \) is the mean porosity of the porous medium initiated by Mueller (2005) (Mueller,
2005) and $c_i, i=1, 2, 3, 4, 5$ are the numerical coefficients obtained from the curve fitting.

Eq. (4.10) change to be $\rho_{\text{max}} = \frac{6}{\pi \sigma^3} (1-c_i)$ when $r_p / \sigma$ tends to be infinite (i.e., bulk phase), so,

$$\sigma = \sqrt[3]{\frac{6(1-c_i)}{\pi \rho_{\text{max}}}} = \sqrt[3]{\frac{6\beta(1-c_i)}{\pi}} = \sqrt[3]{\frac{6(1-c_i)b}{\pi N_A}}$$

where $b$ is the volume parameter of the cubic EOS and $N_A$ is the Avogadro constant.

From the statistical thermodynamics (Abrams and Prausnitz, 1975),

$$P(N, V, T) = kT \left( \frac{\partial \ln Z(N, V, T)}{\partial V} \right)_{N,T}$$

Given that $\frac{1}{N!} \Lambda^{-3N} q_{\text{int}}^N = \text{constant}$, Eq. (4.10) is substituted into Eq. (4.14) to be,

$$P(N, V, T) = kT \left( \frac{\partial \ln [(V - N\beta)^N e^{\int E_{\text{conf}}(N, V, T) dT}]}{\partial V} \right)_{N,T}$$

$$= \frac{NkT}{V - N\beta} - \frac{\partial E_{\text{conf}}(N, V, T)}{\partial V}$$

(4.15)

Since $\beta = \frac{b}{N_A}$ and $N = n \cdot N_A$ from the literature (Abrams and Prausnitz, 1975), the first term right-hand side of Eq. (4.15) is converted to be $\frac{nRT}{V - nb}$, where $n$ denotes the moles. It is easily found from Eq. (4.15) that $E_{\text{conf}}(N, V, T)$ is the key part to explicitly illustrate the relationships of $P, V,$ and $T$. The configurational energy ($E_{\text{conf}}$) is consist of the configurational energy between molecule and molecule ($E_{\text{molecule-molecule}}^{\text{conf}}$) as well as between the molecule and wall ($E_{\text{molecule-wall}}^{\text{conf}}$), which is demonstrated in Figure 4.8 and presented as follows,
Figure 4.8 Schematic diagram of the molecule–molecule and molecule–wall potentials in this study.
\[ E^{\text{conf}}(N,V,T) = E^{\text{conf}}_{\text{molecule-molecule}} + E^{\text{conf}}_{\text{molecule-wall}} \quad (4.16) \]

In this study, the molecule–molecule interactions \( E^{\text{conf}}_{\text{molecule-molecule}} \) are expressed as (Zarragoicoechea and Kuz, 2002),

\[ E^{\text{conf}}_{\text{molecule-molecule}} = \frac{kTN^2}{2V^2} \iiint \frac{U_{mm}(r_1, r_2 \ldots r_N)}{kT} g(r; \rho, T) dV_1 dV_2 dV_3 \]  

(4.17)

where \( g(r; \rho, T) \) is the pair correlation function for molecules interacting through the potential \( U(r) \). In the literature, the pair correlation function at low densities was stated clearly (Islam et al., 2015),

\[ \lim_{\rho \to 0} g(r; \rho, T) = e^{-u(r)/kT} \]  

(4.18)

Here, \( C = C(N,V,T) = \int g(r; \rho, T) dr \). Molecule–molecule interactions \( U_{mm}(r) \) are assumed to be numerically represented through the Lennard-Jones potential, whose schematic diagram is shown in Figure 4.8 and numerical equation is,

\[ U_{mm}(r_{12}) = 4\varepsilon_{\text{LJ}}[\left(\frac{\sigma_{\text{LJ}}}{r_{12}}\right)^{12} - \left(\frac{\sigma_{\text{LJ}}}{r_{12}}\right)^6] \]  

(4.19)

where \( \varepsilon_{\text{LJ}} \) is the molecule–molecule Lennard–Jones energy parameter and \( \sigma_{\text{LJ}} \) is the molecule–molecule Lennard–Jones size parameter.

Thus, Eq. (4.17) is re-written as,

\[ E^{\text{conf}}_{\text{molecule-molecule}} = \frac{kTN^2}{2V^2} \iiint_{r_{12}>\sigma} \frac{U(r_1, r_2 \ldots r_N)}{kT} dV_1 dV_2 \]  

(4.20)

Then, the integral part of Eq. (4.20) is solved analytically as,

\[ \frac{1}{V} \iiint_{r_{12}>\sigma} \frac{U_{mm}(r_1, r_2 \ldots r_N)}{kT} dV_1 dV_2 = \frac{4\varepsilon_{\text{LJ}}}{kT} \sigma_{\text{LJ}}^3 f(A) \]  

(4.21)
\[ f(A) = c_0 + \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \]

where \( c_0 = -\frac{8\pi}{9} \), \( c_1 = 3.5622 \), and \( c_2 = -0.6649 \); and \( A \) is the contact surface area,

\[ A = \pi \left( \frac{r_p}{\sigma} \right)^2. \]

It should be noted that the value of \( c_0 \) was calculated by solving Eq. (4.21) analytically, while the values of \( c_1 \) and \( c_2 \) are obtained from a non-linear least-square method. The calculated \( f(A) \) values from Eq. (4.21) and fitting curve by tuning \( c_1 \) and \( c_2 \) can be found elsewhere (Zarragoicoechea and Kuz, 2002). Thus, the molecule–molecule interactions \( (E_{\text{molecule-molecule}}^{\text{conf}}) \) are presented as,

\[ E_{\text{molecule-molecule}}^{\text{conf}} = \frac{-an^2C + 2n^2C\epsilon_{\text{LJ}}\sigma_{\text{LJ}}^3 \cdot (\frac{c_1}{\sqrt{A}} + \frac{c_2}{A})}{V} \tag{4.22} \]

On the other hand, the molecule–wall interactions \( U_{\text{mw}}(r) \) are assumed to be well modeled through the square-well potential, which is shown in Figure 4.8 and stated as follows,

\[ U_{\text{mw}}(r_{ij}) = \begin{cases} +\infty, & r_{ij} < \sigma_{\text{sw-ij}} \\ -\epsilon_{\text{sw-ij}}, & \sigma_{\text{sw-ij}} \leq r_{ij} \leq (\sigma_{\text{sw-ij}} + \delta_{\text{sw-ij}}) \\ 0, & r_{ij} > (\sigma_{\text{sw-ij}} + \delta_{\text{sw-ij}}) \end{cases} \tag{4.23} \]

where \( r_{ij} \) is the distance between the molecule and wall; \( \epsilon_{\text{sw-ij}} \) is the molecule–wall square-well energy parameter; \( \sigma_{\text{sw-ij}} \) is the molecule–wall square-well size parameter; and \( \delta_{\text{sw-ij}} \) is the molecule–wall square-well width of interactions, which also denotes as \( \delta_p \) to represent the molecule–wall distance in the following sections. Hence, the molecule–wall
interactions \( E_{\text{molecule-wall}}^{\text{conf}} \) are expressed as (Kong and Adidharma, 2018),

\[
E_{\text{molecule-wall}}^{\text{conf}} = -N \cdot F_p \cdot \varepsilon_{sw}
\]  

(4.24)

where \( F_p \) is the fraction of the confined fluid molecules that interact with the pore wall (i.e., in the square-well region). The local distributions of fluid molecules interacting with the pore wall are numerically represented by \( F_p \), which is function of the temperature, fluid density, degree of confinement, and molecule-wall interaction potential (Sandler, 1985). An empirical correlation rather than a complex theoretical model is capable of describing \( F_p \) in an accurate and simple way as follows,

\[
F_p = F_{pr} + (1 - F_{pr})(1 - e^{-\varepsilon_{sw}/kT})(1 - \frac{\rho}{\rho_{\text{max}}})^\theta
\]

(4.25)

\[
F_{pr} = \frac{(r_p - \sigma / 2)^2 - (r_p - \sigma / 2 - \delta_p)^2}{(r_p - \sigma / 2)^2}
\]

\[
\theta = \frac{r_p}{\delta_p + \sigma / 2}
\]

where \( F_{pr} \) is the fraction of the random distributed fluid molecules in the square-well region of the pores and \( \theta \) is the geometric term. Thus, Eq. (4.25) is substituted into Eq. (4.24) to be,

\[
E_{\text{molecule-wall}}^{\text{conf}} = -n \cdot N_A \cdot \varepsilon_{sw} \left[ F_{pr} + (1 - F_{pr})(1 - e^{-\varepsilon_{sw}/kT})(1 - \frac{\rho}{\rho_{\text{max}}})^\theta \right]
\]

(4.26)

\[
\rho = \frac{N}{V}, \rho_{\text{max}} = \frac{N_A}{b}
\]

where \( \rho \) is the volume number density. Hence, the total configurational energy between molecule and molecule as well as between the molecule and wall is obtained by combing
Eqs. (4.16), (4.22), and (4.26),

\[
E^{\text{conf}}(N, V, T) = -\frac{an^2C + 2n^2CE_{LJ}^3\sigma_{LJ}^3(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A})}{V} - n \cdot N_A \cdot \varepsilon_{sw} [F_{pr} + (1 - F_{pr})(1 - e^{-\varepsilon_{sw}/kT})(1 - \frac{nb}{V})^\theta]
\]

(4.27)

Here, \(C\) is treated as a constant. On a basis of Eq. (4.15), the generalized expression of the EOS for confined fluids considering the effects of pore radius, molecule–molecule, and molecule–wall interactions is shown as,

\[
P(N, V, T) = \frac{nRT}{V - nb} - \frac{n^2}{V^2}[a - 2E_{LJ}\sigma_{LJ}^3(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A})] + (nN_A \cdot \varepsilon_{sw})(\frac{nb\theta}{V^2})(1 - \frac{nb}{V})^{\theta-1}(1 - F_{pr})(1 - e^{-N_A\varepsilon_{sw}/RT})
\]

(4.28)

**Phase equilibrium calculations**

The newly-developed generalized EOS in nanopores from Eq. (4.28) is applied to calculate the vapour–liquid equilibrium (VLE) in this study. The initial \(K\)-value of each component can be estimated from Wilson’s equation (Wilson, 1964),

\[
K_i = \frac{P_i}{P} \exp[5.37(1 + \omega_i)(1 - \frac{T_i}{T})]
\]

(4.29)

where \(P_i\) is the critical pressure of component \(i\); \(T_i\) is the critical temperature of component \(i\); \(\omega_i\) is the acentric factor of component \(i\). Then the Rachford–Rice equation is applied to calculate \(x_i\) and \(y_i\),

\[
\sum_{i=1}^{n} \frac{z_i(K_i - 1)}{1 + (K_i - 1)\beta} = 0
\]

(4.30)

where \(\beta\) is the vapour fraction.

The compressibility of the liquid or vapour phase can be determined,
\[
Z_L^3 - (1 + B_L)Z_L^2 + \left[ A_L - \frac{B_L \theta}{RT} (N_A \cdot \epsilon_{sw})(1 - \frac{b}{V})^{\theta-1}(1 - F_{pr})(1 - e^{-N_A \epsilon_{sw}/RT})\right] Z_L \\
\quad - [A_L B_L - \frac{B_L^2 \theta}{RT} (N_A \cdot \epsilon_{sw})(1 - \frac{b}{V})^{\theta-1}(1 - F_{pr})(1 - e^{-N_A \epsilon_{sw}/RT})] = 0
\]

(4.31a)

\[
Z_V^3 - (1 + B_V)Z_V^2 + \left[ A_V - \frac{B_V \theta}{RT} (N_A \cdot \epsilon_{sw})(1 - \frac{b}{V})^{\theta-1}(1 - F_{pr})(1 - e^{-N_A \epsilon_{sw}/RT})\right] Z_V \\
\quad - [A_V B_V - \frac{B_V^2 \theta}{RT} (N_A \cdot \epsilon_{sw})(1 - \frac{b}{V})^{\theta-1}(1 - F_{pr})(1 - e^{-N_A \epsilon_{sw}/RT})] = 0
\]

(4.31b)

where \( Z_L \) and \( Z_V \) are the respective compressibility factors of the liquid and vapour phases;

\[
A_L = \frac{P_L}{R^2T^2} \left[ a - 2 \epsilon_{Lj} \alpha_{Lj} \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right) \right], \quad B_L = \frac{b P_L}{RT}, \quad A_V = \frac{P_V}{R^2T^2} \left[ a - 2 \epsilon_{Lj} \alpha_{Lj} \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right) \right], \quad B_V = \frac{b P_V}{RT}.
\]

Constants of \( a \) and \( b \) are obtained by applying the van der Waals mixing rule,

\[
a = \sum_{i} \sum_{j} x_i x_j a_{ij}
\]

(4.32a)

\[
b = \sum_{i} x_i b_i
\]

(4.32b)

where \( a_{ij} \) is the binary interaction of component \( i \) and component \( j \), \( a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \);

\( k_{ij} \) is the binary interaction coefficient of component \( i \) and component \( j \); \( k_{ii} = k_{jj} = k_{ij} \) and \( k_{ij} = k_{ji} = 0 \). Minimum Gibbs free energy is applied to select roots of the compressibility factors for the liquid and vapour phases (Whitson and Brule, 2000).

The liquid and vapour phases are assumed to be the wetting phase and non-wetting phase, respectively (Nojabaie et al., 2013). Thus the capillary pressure \( (P_{cap}) \) is,

\[
P_{cap} = P_V - P_L
\]

(4.33)

where \( P_V \) is the pressure of the vapour phase and \( P_L \) is the pressure of the liquid phase. On the other hand, the capillary pressure can be expressed by Young–Laplace equation,
\begin{equation}
\frac{P_{\text{cap}}}{r_p} = \frac{2\gamma}{r_p} \cos \phi
\end{equation}

where \( \gamma \) is the interfacial tension and \( \phi \) is the contact angle of the vapour–liquid interface with respect to the pore surface, which is assumed to be 30° according to the experimental results in the literature (Wang et al., 2014). Therein, the IFT is estimated by means of the Macleod–Sugden equation, which will be specifically introduced in the next section.

The fugacity of a mixture is,

\begin{equation}
\ln f_i^L = \ln\left(\frac{n_i RT}{V_L - nb}\right) + \frac{nb_i}{V_L - nb} - \frac{2\sum_{ij} n_{ij}}{RTV_L} \left[a - 2\epsilon_{iL} \sigma_{ij}^3 \left(\frac{c_i}{\sqrt{A}} + \frac{c_2}{A}\right)\right]
- \frac{N_i \epsilon_{\text{sys}}}{RT} (1 - F_p)(1 - e^{-N_i \epsilon_{\text{sys}} / RT}) \left[\left(1 - \frac{nb_i}{V_L}\right)^{\theta - 1} \cdot \frac{nb_i \theta}{V_L^2} \cdot \frac{2V_L - nb(\theta - 1)}{V_L - nb}\right]
\end{equation}

\begin{equation}
\ln f_i^V = \ln\left(\frac{n_i RT}{V_v - nb}\right) + \frac{nb_i}{V_v - nb} - \frac{2\sum_{ij} n_{ij}}{RTV_v} \left[a - 2\epsilon_{iL} \sigma_{ij}^3 \left(\frac{c_i}{\sqrt{A}} + \frac{c_2}{A}\right)\right]
- \frac{N_i \epsilon_{\text{sys}}}{RT} (1 - F_p)(1 - e^{-N_i \epsilon_{\text{sys}} / RT}) \left[\left(1 - \frac{nb_i}{V_v}\right)^{\theta - 1} \cdot \frac{nb_i \theta}{V_v^2} \cdot \frac{2V_v - nb(\theta - 1)}{V_v - nb}\right]
\end{equation}

The VLE calculations based on the modified EOS require a series of iterative computation through, for example, the Newton–Raphson method. The flowchart of the VLE calculation process can be found in the previous study (Zhang et al., 2017b).

**IFT calculations in nanopores**

The parachor model is most commonly used by the energy industry to predict the IFT of a liquid–vapour (e.g., crude oil–CO₂) system (Nobakht et al., 2008). Macleod first related the surface tension between the liquid and vapour phases of a pure component to its parachor and the molar density difference between the two phases (Macleod, 1923),

\[ \sigma = [p(\rho_L - \rho_V)]^4 \]

where \( \sigma \) is the surface tension in mJ/m²; \( p \) is the parachor.
At a later time, Eq. (4.36) was extended to a multi-component mixture, which is the so-called Macleod–Sugden equation (Sugden, 1924),

$$\gamma = \left( \rho_L \sum_{i=1}^{r} x_i p_i - \rho_v \sum_{i=1}^{r} y_i p_i \right)^4$$  \hspace{1cm} (4.37)

where $\gamma$ is the IFT between the vapour and liquid bulk phases of the multi-component mixture; $x_i$ and $y_i$ are the respective mole percentages of the $i^{th}$ component in the liquid and vapour bulk phases, $i = 1, 2, \ldots, r$; $r$ is the component number in the mixture; and $p_i$ is the parachor of the $i^{th}$ component. Since $\rho_L = \frac{p_i MW_L}{Z_L RT}$, and $\rho_v = \frac{p_v MW_v}{Z_v RT}$, Eq. (4.37) is rewritten as,

$$\gamma = \left( \frac{p_i MW_L}{Z_L RT} \sum_{i=1}^{r} x_i p_i - \frac{p_v MW_v}{Z_v RT} \sum_{i=1}^{r} y_i p_i \right)^4$$  \hspace{1cm} (4.38)

where $MW_L$ is the molecular weight of the liquid phase and $MW_v$ is the molecular weight of the vapour phase. The parachor model coupled with the generalized EOS is applied for calculating the confined fluid IFT in nanopores.

4.2.4 Results and discussion

Phase behaviour in bulk phase and nanopores

The proposed VLE calculation model based on the newly-developed generalized EOS is applied to calculate the phase behaviour for different pure and mixing HCs in bulk phase and nanopores, whose results are compared with and verified by the measured data. Table 4.3 shows the measured (Zhang and Gu, 2015) and calculated saturation pressures, liquid densities, and liquid SFs of the mixing hydrocarbon A–pure CO$_2$ systems at the temperature of $T = 53.0^\circ$C. It is found from the table that the calculated data agree well with the
measured PVT data since their relative errors are rather small. The relative errors between the measured and calculated data increase with more CO₂ dissolutions. This is because the binary interaction coefficients (BICs) between CO₂ and hydrocarbons are obtained from the empirical correlation (Whitson and Brule, 2000), which may be unable to represent the actual mutual interactions to some extent.

In nanopores, the phase behaviour measurements are always targeted on some simple mixing HCs due to the relatively lower experimental requirements and more simplified physiochemical mechanisms (Alfi et al., 2016; L. Liu et al., 2018b). Figures 4.9a and b show the measured (Cho et al., 2017) and calculated pressure–volume (P–V) curves for the CH₄–C₁₀H₂₂ systems at the pore radii of \( r_p = 3.5 \) and 3.7 nm and temperatures of \( T = 38 \) and 52 °C. The calculated P–V curves are in good agreement with the measured results in the two figures, where the volume is increased with the pressure decrease. The pressures at \( r_p = 3.5 \) nm are always lower than those at \( r_p = 3.7 \) nm due to an enhanced confinement effect. Obviously, a temperature increase leads the bubble-point pressures to be increased in comparison with the lower temperature case. Moreover, the calculated pressure differences between the 3.5 and 3.7 nm cases are reduced at a higher temperature. This may be attributed to the large temperature increase from 38 to 52 °C, which dominates the phase behaviour change so that the effect of the relatively small pore radius reduction become negligible. Furthermore, the measured and calculated PVT data for the \( iC₄H₁₀–nC₄H₁₀–C₈H₁₈ \) system before and after flash calculations at two different conditions (i.e., constant pressure and constant temperature) are obtained from the literature (Wang et al., 2014) and summarized in Table 4.4. In a similar manner with the previous study, the lighter components (i.e., \( iC₄ \) and \( nC₄ \)) prefer to be in the vapour phase by increasing the
Figure 4.9a Measured (Cho et al., 2017) and calculated pressure–volume curves for the CH$_4$–C$_{10}$H$_{22}$ systems at the pore radii of $r_p = 3.5$ and 3.7 nm and $T = 38$ °C.
Figure 4.9b Measured (Cho et al., 2017) and calculated pressure–volume curves for the CH$_4$–C$_{10}$H$_{22}$ systems at the pore radii of $r_p = 3.5$ and 3.7 nm and $T = 52$ °C.
temperature or reducing the pressure. Overall, the calculated compositions and fractions of
the liquid and vapour phases, IFTs, as well as the capillary pressure are found to agree well
with the measured data. Thus, the proposed VLE calculation model based on the new
generalized EOS is capable of calculating the phase behaviour of the pure and mixing HC
systems in bulk phase and nanopores in an accurate manner.

**Calculated interfacial tensions in nanopores**

The proposed model based on the new generalized EOS is applied to calculate the IFTs
of four different pure and mixing HC systems at different conditions. It is worthwhile to
mention that in this study, the respective FGLR, pore radius, and square-well width (i.e.,
wall-effect distance) not specially mentioned are always set to be 0.9:0.1, 10 nm, and 1 nm,
respectively. The reasons for choosing these three values can be referred in the literature
(Zhang et al., 2018e; Zhang et al., 2017a).

Figures 4.10a and b show the calculated IFTs of the CO\textsubscript{2}–C\textsubscript{10}H\textsubscript{22} and CH\textsubscript{4}–C\textsubscript{10}H\textsubscript{22}
systems in bulk phase and nanopores of 10 nm from the original and modified PR EOS
(Zhang et al., 2017a) as well as the new model at the temperature of $T = 53.0 \, ^\circ C$. It is found
from these figures that the calculated IFTs in bulk phase or nanopores are always decreased
with the pressure increase. More specifically, two distinct pressure range, a drastic IFT
reduction at low pressures but a much gradual or even constant IFT change at high
pressures, occur in the CO\textsubscript{2}–C\textsubscript{10}H\textsubscript{22} system, whereas the CH\textsubscript{4}–C\textsubscript{10}H\textsubscript{22} IFTs are almost
linearly decreased but at a much slow rate. This is because in comparison with CO\textsubscript{2}, CH\textsubscript{4}
has a much lower solubility in the liquid C\textsubscript{10}H\textsubscript{22} and a rather weaker ability for liquid HC
extractions (Zhang et al., 2018e). Hence, the two-way mass transfer, which contributes to
the IFT reduction to a large extent (Janiga et al., 2018), is substantially weakened for the
Table 4.4

Measured (Wang et al., 2014) and calculated pressure–volume–temperature data for $iC_4H_{10}–nC_4H_{10}–C_8H_{18}$ system in the micro-channel of 10 μm and nano-channel of 100 nm at (a) constant pressure and (b) constant temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before flash calculation (Wang et al., 2014)</th>
<th>After flash calculation (Wang et al., 2014)</th>
<th>After flash calculation (this study)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) constant pressure case</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>24.9</td>
<td>71.9</td>
<td></td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>85,260</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid ($iC_4–nC_4–C_8$, mol.%)</td>
<td>15.47</td>
<td>4.53</td>
<td>80.00</td>
</tr>
<tr>
<td>Vapour ($iC_4–nC_4–C_8$, mol.%)</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Liquid fraction (mol.%)</td>
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<td>83.98</td>
</tr>
<tr>
<td>Vapour fraction (mol.%)</td>
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<td>16.02</td>
</tr>
<tr>
<td>IFT (mJ/m$^2$)</td>
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<td>16.98</td>
</tr>
<tr>
<td>$P_{cap}$ in micro-channel (kPa)</td>
<td>–</td>
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<td>3.01</td>
</tr>
<tr>
<td>$P_{cap}$ in nano-channel (kPa)</td>
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<td>(b) constant temperature case</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (Pa)</td>
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<td>Vapour fraction (mol.%)</td>
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<tr>
<td>$P_{cap}$ in nano-channel (kPa)</td>
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<td>235.54</td>
<td>221.39</td>
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Figure 4.10a Calculated interfacial tensions of the CO$_2$–C$_{10}$H$_{22}$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C.
Figure 4.10b Calculated interfacial tensions of the CH$_4$–C$_{10}$H$_{22}$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C.
CH$_4$–C$_{10}$H$_{22}$ system so that their corresponding IFTs are higher than those of the CO$_2$–C$_{10}$H$_{22}$ system, especially at high pressures.

Obviously, at low pressures, the calculated IFTs in nanopores from the new model in this study are always lower than the IFTs in bulk phase but higher than those in nanopores from the modified PR EOS (Zhang et al., 2017a). The reasons why the calculated IFTs are lower in nanopores compared to those in bulk phase have been clearly explained in the previous study (Teklu et al., 2014b; Zhang et al., 2017b). In a word, some phenomena, such as capillary pressure and shifts of critical properties, can be significantly enhanced under the confinement effect, which overall lead the IFTs to be lower in nanopores. On the other hand, the calculated IFTs in nanopores from the modified PR EOS in the previous study are different from the results of the new model. It should be noted that the modified PR EOS mainly considers the enhanced capillary pressure and shifts of critical properties (Zhang et al., 2017a), whereas the new model takes account for, in addition to the two above-mentioned phenomena, the molecule–molecule and molecule–wall interactions. In this case, the molecule–wall interaction may be weak because the wall-effect distance (1nm) is relatively smaller than the pore radius (10 nm). However, the repulsive molecule–molecule interactions are strong and prevent the fluid to be mutually soluble so that the calculated IFTs from the new model are always higher. The aforementioned patterns are observed from the figures for either the CO$_2$–C$_{10}$H$_{22}$ or CH$_4$–C$_{10}$H$_{22}$ systems at low pressures but tend to be different at high pressures. The calculated IFTs of the CO$_2$–C$_{10}$H$_{22}$ system are almost equivalent in bulk phase and nanopores at high pressures. In Figure 4.10b, the calculated IFTs in nanopores are even higher than those in bulk phase at high pressures. This is because the confinement effect-induced phenomena, especially the
molecule–molecule interactions, are considerably strengthened with the pressure increase. The miscible state of the liquid–gas system may be achieved in bulk phase at some high pressure, meanwhile, the fluid system is still in two distinct phases in nanopores under the strong effect of the molecule–molecule interactions so that a higher IFT is obtained. It is apparent that the confinement effect on the two-way mass transfer and IFTs of the simple HC systems at high pressures is magnified by adding some lean gas (e.g., CH₄) into the system, which can be clearly evaluated by means of the new model.

In Figures 4.11a and 4.12a, the calculated IFTs of the mixing HCs A and B–pure CO₂ systems in bulk phase and nanopores of 10 nm from the original and modified PR EOS as well as the new model at the FGLR of 0.9:0.1 and $T = 53.0 \, ^\circ\text{C}$ are shown. It is seen from the figures that the calculated IFTs of the mixing HC B–pure CO₂ system in bulk phase and nanopores are always higher than those of the A case. This is because a larger quantity of CH₄, around 36.74%, is contained in the mixing HC B while no CH₄ exists in the mixing HC A. As aforementioned that CH₄ is a lean gas and detrimental to the mutual interactions so that the corresponding IFTs become higher. The calculated IFTs of both two mixing HC–pure CO₂ systems from the new model are lower than those in bulk phase but higher than those from the modified PR EOS in nanopores, whose technical explanations have been specified in the previous paragraph. In a similar pattern with the above-mentioned two simple HC systems, the calculated IFTs of the mixing HC A–pure CO₂ system in bulk phase and nanopores are almost same while the mixing HC B–pure CO₂ IFTs in nanopores are higher than those in bulk phase at high pressures. Thus, the confinement effect on the IFTs of the mixing HC systems is also magnified by adding some lean gas (e.g., CH₄). It is inferred that the resultant effects of the confinement and composition are strong enough to
Figure 4.11a Calculated interfacial tensions of the mixing hydrocarbon A–pure CO₂ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C and feed gas to liquid ratio of 0.9:0.1 in mole fraction.
Figure 4.11b Calculated interfacial tensions of the mixing hydrocarbon A–pure CO$_2$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C and feed gas to liquid ratio of 0.7:0.3 in mole fraction.
Figure 4.11c Calculated interfacial tensions of the mixing hydrocarbon A–pure CO₂ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0 \, ^\circ C$ and feed gas to liquid ratio of 0.5:0.5 in mole fraction.
Figure 4.11d Calculated interfacial tensions of the mixing hydrocarbon A–pure CO$_2$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C and feed gas to liquid ratio of 0.3:0.7 in mole fraction.
Figure 4.11e Calculated interfacial tensions of the mixing hydrocarbon A–purity CO$_2$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C and feed gas to liquid ratio of 0.1:0.9 in mole fraction.
Figure 4.12a Calculated interfacial tensions of the mixing hydrocarbon B–pure CO₂ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C and feed gas to liquid ratio of 0.9:0.1 in mole fraction.
Figure 4.12b Calculated interfacial tensions of the mixing hydrocarbon B–pure CO₂ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of \( T = 53.0 \, ^{\circ}C \) and feed gas to liquid ratio of 0.7:0.3 in mole fraction.
Figure 4.12c Calculated interfacial tensions of the mixing hydrocarbon B–pure CO₂ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0 \, ^{\circ}\text{C}$ and feed gas to liquid ratio of 0.5:0.5 in mole fraction.
**Figure 4.12d** Calculated interfacial tensions of the mixing hydrocarbon B–pure CO$_2$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0 \, ^\circ\text{C}$ and feed gas to liquid ratio of 0.3:0.7 in mole fraction.
Figure 4.12e Calculated interfacial tensions of the mixing hydrocarbon B–pure CO₂ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at the temperature of $T = 53.0$ °C and feed gas to liquid ratio of 0.1:0.9 in mole fraction.
take effect on the phase behaviour and IFT changes at high pressures.

**Four important factors**

Four important factors, the FGLR, temperature, pore radius, and wall-effect distance, are studied to evaluate their effects on the IFTs in nanopores.

*Feed gas to liquid ratio*

The FGLR effects on the IFTs of the pure and mixing HC systems in bulk phase and nanopores are demonstrated in Figures 4.10–4.12. Although the calculated IFTs of the CO$_2$–C$_{10}$H$_{22}$ and CH$_4$–C$_{10}$H$_{22}$ systems have been specifically analyzed in the previous section, it is still worthwhile to mention that the calculated IFTs of these two simple HC systems keep same at different FGLRs. Hence, one unique figure for each system (i.e., Figures 4.10a and b) is listed even though the corresponding IFTs at five different FGLRs of 0.9:0.1–0.1:0.9 in mole fraction have been calculated. An absolutely different situation in terms of the FGLR effect on the IFTs is obtained for the mixing HC case. Figures 4.11a–e and 4.12a–e show the calculated IFTs of the mixing hydrocarbon A and B–pure CO$_2$ systems in bulk phase and nanopores of 10 nm at $T = 53.0$ °C and five different FGLRs of 0.9:0.1–0.1:0.9 in mole fraction. First, the calculated IFTs in bulk phase and nanopores at different FGLRs follow the same patterns what have been above-mentioned. Second, it is depicted from the figures that either the calculated IFTs in bulk phase or in nanopores are decreased by reducing the FGLR. It should be noted that from Figures 4.11c–e, the calculated IFTs in bulk phase suddenly drop to zero at some pressure. This is because the feed gas is totally dissolved into the liquid phase, which is not enough to saturate the liquid phase but a single phase has already be formed. The detailed explanations about this phenomenon can be found in the previous study (Zhang et al., 2018e). Third, the differences of the calculated IFT in nanopores from the modified PR EOS and new model
are decreased with the FGLR reduction. It is inferred that the gaseous/light HC component induced molecule–molecule and molecule–wall interactions are weakened with less feed gas (i.e., a reduced FGLR) so that the calculated IFTs from these two methods become closer at low pressures and even equivalent at high pressures. Thus, it is always suggested to reduce the FGLR in order to have a lower mixing HC IFTs in bulk phase and nanopores.

**Temperature**

In Figures 4.13a–c, the calculated IFTs of the mixing hydrocarbon A–pure CO$_2$ system at five different temperatures of $T = 15.6$, 30.0, 53.0, 80.0, and 116.1 °C in bulk phase and nanopores of 10 nm are plotted versus the pressure. Overall, the calculated IFTs in nanopores from the new model are lower than those in bulk phase but higher than the IFTs from the modified PR EOS at any temperature. Moreover, the calculated IFTs in bulk phase and nanopores are reduced with the temperature increase at low pressures but increase at high pressures. It is found from Figure 4.13a that the above-mentioned change occurs at some pressures of 5–7 MPa, which coincidently roughly equals to the CO$_2$ critical pressure (Zhang et al., 2018e). Thus, the gaseous CO$_2$–mixing HC IFTs in bulk phase are inferred to be lowered by increasing the temperature while the liquid/supercritical CO$_2$–mixing HC IFTs may be increased at higher temperatures. In nanopores, the pattern-change pressures are reduced to lower values from Figures 4.13b and c, which make sense and still agree well with the CO$_2$ critical pressure because the critical properties of the confined fluids have been proven to shift to lower values in nanopores (Zhang et al., 2018a). In addition, the degrees of the temperature effect on the IFTs in bulk phase and nanopores are different. By comparing these three figures, it is easily found that the temperature effects on the IFTs are weakened in nanopores. However, the degrees of temperature effect on the calculated
Figure 4.13a Calculated interfacial tensions of the mixing hydrocarbon A–pure CO₂ system at five different temperatures in bulk phase from the original Peng–Robinson equations of state (PR EOS).
Figure 4.13b Calculated interfacial tensions of the mixing hydrocarbon A–pure CO₂ system at five different temperatures in nanopores of 10 nm from the modified PR EOS (Zhang et al., 2017a).
Figure 4.13c Calculated interfacial tensions of the mixing hydrocarbon A–pure CO$_2$ system at five different temperatures in nanopores of 10 nm from the new model in this study.
IFTs in nanopores from the modified PR EOS and new model are different. The molecule–molecule and molecule–wall interactions are more easily affected by the temperature change so that the corresponding calculated IFTs are changeable at different temperatures. Six different pressures are selected in order to better study the temperature effect on the IFTs. Figures 4.14a–f show the calculated IFTs of the mixing HC A–pure CO$_2$ system in nanopores at the five different temperatures and six different pressures of $P = 1.0, 4.0, 8.5, 10.5, 15.0, \text{ and } 25.0$ MPa. More specifically, at low pressures like $P = 1.0$ MPa, both IFTs in bulk phase and nanopores are reduced with the temperature increase. The IFTs in bulk phase still follow the trend that to be decreased by increasing the temperature at $P = 4.0$ MPa, whereas the IFTs in nanopores slightly change with the temperature increase. Once the pressure is increased to be higher than the CO$_2$ critical pressure, $P = 8.5, 10.5, 15.0, \text{ and } 25.0$ MPa, the IFTs in bulk phase and nanopores are increased with the temperature increase. However, the IFT variations become smaller with the pressure increase, which means the temperature effect on the IFTs in bulk phase and nanopores become weaker at higher pressures. It is found from the figures that in comparison with the IFTs in nanopores, the IFTs in bulk phase are affected by the temperature variations to a larger extent at any pressures. Only at extremely high pressures like $P = 25.0$ MPa, the temperature effects on the IFTs in bulk phase and nanopores are almost equivalent. Furthermore, the IFTs in nanopores from the new model considering the molecule–molecule and molecule–wall interactions are always higher than those from the modified PR EOS, whose differences are reduced with the pressure increase. It means at extremely high pressures, the IFTs are less affected by the temperature, pore radius, or confinement but dominated by the pressure effect.
Figure 4.14 Calculated interfacial tensions of the mixing hydrocarbon A–pure CO$_2$ system in bulk phase and nanopores of 10 nm from the original and modified Peng–Robinson equations of state (Zhang et al., 2017a) as well as the new model in this study at five different temperatures and pressures of (a) $P = 1.0$ MPa; (b) $P = 4.0$ MPa; (c) $P = 8.5$ MPa; (d) $P = 10.5$ MPa; (e) $P = 15.0$ MPa; and (f) $P = 25.0$ MPa.
Pore radius and wall-effect distance

Effects of the pore radius and wall-effect distance on the IFTs cannot be evaluated by means of the original PR EOS, thus, the modified PR EOS and new model are applied to calculate the IFTs of the mixing HC A–pure CO₂ system at $T = 53.0$ °C and six different pore radii of $r_p = 1000, 100, 10, 5, 1,$ and 0.1 nm, whose results are shown in Figures 4.15a and b, respectively. It is found from Figure 4.15a that the calculated IFTs from the modified PR EOS are monotonically decreased by reducing the pore radius. The IFTs at $r_p = 1000$ and 100 nm are relatively higher than the IFTs at other smaller pore radii. Although the IFTs are generally reduced with the reduction of pore radius at $r_p \leq 10$ nm, which become almost equivalent at very high pressures. The calculated IFTs from the new model considering the molecule–molecule and molecule–wall interactions are plotted versus the pressure at the six different pore radii in Figure 4.15b, which are compared with the measured IFTs for the same system in bulk phase. It is found that the calculated IFTs at $r_p = 1000$ nm agree well with the measured IFTs. It is seen from Figure 4.15b that the calculated IFTs follow a similar pattern with Figure 4.15a but at relatively higher values down to $r_p = 5$ nm. This is because the molecule–molecule interactions are strengthened at $r_p \leq 100$ nm. At $r_p = 1$ and 0.1 nm, the IFTs at low pressures also share a similar pattern with the above-mentioned case, whereas the IFTs at high pressures become higher than those at larger pore radii of $r_p = 10$ and 5 nm and even slightly lower than those at $r_p = 1000$ and 100 nm. This abnormal phenomenon is attributed to the consideration of the molecule–wall interactions in the new model. It is worthwhile to mention that the wall-effect distance (i.e., square-well width) is set to be 1 nm in all aforementioned calculations, which means the wall-effect region occupies the nanopore when the pore radius is reduced
Figure 4.15a Measured (Zhang and Gu, 2016b) and calculated interfacial tensions of the mixing hydrocarbon A–pure CO$_2$ system at the temperature of $T = 53.0$ °C and six different pore radii in nanopores from the modified Peng–Robinson equation of state.
Figure 4.15b Measured (Zhang and Gu, 2016b) and calculated interfacial tensions of the mixing hydrocarbon A–pure CO₂ system at the temperature of $T = 53.0 \, ^\circ C$ and six different pore radii in nanopores from the new model in this study.
to 1 nm. In this case, the molecule–wall interaction dominates the IFTs at either low or high pressures so that the abnormal IFT trends are observed.

In order to clearly evaluate and better understand the effects of pore radius and wall-effect distance on the IFTs, the calculated IFTs of the same system in nanopores at $T = 53.0$ °C, pore radii of $r_p = 1000–0.1$ nm, wall-effect distances of $\delta_p = 10–0.001$ nm, six different pressures of $P = 1.0, 4.0, 8.5, 10.5, 15.0,$ and $18.0$ MPa are shown in Figures 4.16a–f. It is found from the figures that the IFTs from both two models are reduced with the pore radius reduction at $P \leq 10.5$ MPa, wherein the IFT variations from the modified PR EOS are always larger than those from the new model, especially at $r_p \leq 100$ nm, and the IFTs from the new model are almost constant at $r_p \leq 1$ nm under the wall effect. The IFTs from the modified PR EOS still follow the similar trend at high pressures (e.g., $P = 15.0$ and $18.0$ MPa), whereas IFTs of the new model case have abnormal increases at $1 \text{ nm} \leq r_p \leq 5 \text{ nm}$ and tend to be constant at $r_p \leq 1$ nm. The phenomenon is attributed to the addition of the molecule–molecule and molecule–wall interactions into the new model. The medium-dashed line in each figure represents the calculated IFTs from the new model with respect to the ratio of wall-effect distance to pore radius ($\delta_p / r_p$). The calculated IFTs are decreased by increasing the ratio up to $\delta_p / r_p = 1.0$ at any pressures except for $P = 15.0$ and $18.0$ MPa, after which the IFTs are almost constant. This is because the wall effect is relatively weak so that the other confinement-induced phenomena dominate the IFT changes when $\delta_p / r_p < 1.0$. Once the wall-effect distance is equal to or even larger than the pore radius, the wall-effect region absolutely occupies the nanopores so that any change of $\delta_p$ won’t make any difference on the IFTs.

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Figure 4.16 Calculated interfacial tensions of the mixing hydrocarbon A–pure CO₂ system in nanopores from the modified Peng–Robinson equations of state (Zhang et al., 2017a) and the new model in this study at the temperature of $T = 53.0 \, ^\circ\text{C}$, different pore radius with different wall-effect distances, and pressures of (a) $P = 1.0 \, \text{MPa}$; (b) $P = 4.0 \, \text{MPa}$; (c) $P = 8.5 \, \text{MPa}$; (d) $P = 10.5 \, \text{MPa}$; (e) $P = 15.0 \, \text{MPa}$; and (f) $P = 18.0 \, \text{MPa}$.
4.3 Summary

In Part I, the equilibrium two-phase compositions are predicted and analyzed to elucidate the pressure dependence of the equilibrium interfacial tensions (IFTs) of three different light crude oil–CO\(_2\) systems. The predicted equilibrium IFTs of the three light crude oil–CO\(_2\) systems are found to be in good agreement with the measured IFTs. The predicted IFT is slightly lower at a relatively higher pressure, which is because the light crude oil is not completely and accurately characterized in the PR-EOS modeling. For example, no heavy aromatic or asphaltic components are considered. It is found that CO\(_2\) dissolution is a dominant mass-transfer process, which accounts for 90\% of the total compositional change. Moreover, three pressure ranges are identified and explained in the equilibrium two-phase compositions vs. pressure curves. Furthermore, the density difference between the crude oil and gas phases is a key factor in the parachor model for the IFT predictions. The equilibrium IFT vs. pressure curve is found to have the same three pressure ranges, which are attributed to the initial gas dissolution and compression, the subsequent strong HCs-extraction, and the final weak HCs-extraction, respectively. The initial oil and gas compositions have direct effects on the two-way mass transfer and affect the equilibrium IFT variations to different extents. The initial gas composition is proven to have a stronger effect on the equilibrium IFTs than the initial oil composition. The initial gas fraction effect is found to be weak for the dead light crude oil–pure and impure CO\(_2\) systems. However, the equilibrium IFT of the live light crude oil–pure CO\(_2\) system at a low initial gas fraction is lower at a lower equilibrium pressure but it becomes higher at a higher equilibrium pressure. Last but not least, the miscibility of the dead light crude oil–pure/impure CO\(_2\) system can be achieved at the initial gas mole fractions of > 0.70 and
at certain threshold pressure. Otherwise, it is the complete pure/impure CO\textsubscript{2} dissolution into the dead light crude oil that leads to zero IFT in either system at the initial gas mole fractions of ≤ 0.70.

In Part II, confined fluid IFTs in nanopores and their influential factors are comprehensively studied. First, a new generalized EOS, which considers the pore radius effect, intermolecular interaction, and wall effect, is developed in the analytical formulation for calculating the thermodynamic phase behaviour of confined pure and mixing fluids in nanopores. Then, the newly-developed model based on the generalized EOS and coupled with the parachor model, which is also fully capable of modeling the capillary pressure and shifts of critical properties in addition to the above-mentioned confinement effects, is found to be accurate for vapour–liquid equilibrium (VLE) and IFT calculations in bulk phase and nanopores. The IFTs in bulk phase of the pure and mixing hydrocarbon (HC) systems are always higher than those in nanopores. At low pressures, the calculated IFTs from the new model are higher than those from the modified PR EOS, whereas they become almost equivalent at high pressures. The confinement effect on the IFTs of the simple or mixing HC systems is magnified by adding some lean gas (e.g., CH\textsubscript{4}) and the resultant effects of the confinement and composition are strong enough to take effect on the phase behaviour and IFT changes at high pressures. The calculated IFTs of the simple HC systems (i.e., CO\textsubscript{2}–C\textsubscript{10}H\textsubscript{22} and CH\textsubscript{4}–C\textsubscript{10}H\textsubscript{22} systems) in nanopores keep constant at different FGLRs. In a mixing HC system, the calculated IFTs in nanopores are decreased by reducing the FGLRs. The gaseous CO\textsubscript{2}–mixing HC IFTs in bulk phase and nanopores are inferred to be lowered by increasing the temperature at low pressures while the liquid/supercritical CO\textsubscript{2}–mixing HC IFTs may be increased at higher temperatures. The temperature effect on the
IFTs are weakened in nanopores at most pressure, which become almost the same with bulk phase case at extremely high pressures. Finally, the IFTs in nanopores are generally decreased with the reduction of pore radius but keep constant at $\delta_p / r_p \geq 1.0$. This is because the wall effect is relatively weak so that the other confinement-induced phenomena dominate the IFT changes when $\delta_p / r_p < 1.0$. Once the wall-effect region absolutely occupies the nanopores (i.e., $\delta_p / r_p \geq 1.0$), any change of $\delta_p$ won’t cause any difference in terms of the IFTs.
CHAPTER 5  MINIMUM MISCIBILITY PRESSURE DETERMINATIONS

5.1  Introduction

Gas injection, for example, CO₂, CH₄, or N₂, has been proven to be the most effective and promising enhanced oil recovery (EOR) technique for recovering light to medium oils worldwide (Mokhtari et al., 2014). A miscible gas displacement is always desired for a successful gas injection project because higher oil recovery factors can be reached from the gas injection at the miscible state. In theory, an oil recovery factor of 100% can be achieved under the miscible state in homogeneous porous media (Chen et al., 2017). Accordingly, the minimum miscibility pressure (MMP) is defined as the lowest operating pressure at which the oil and gas phases can become miscible in any portions through a dynamic multi-contact miscibility (MCM) process at the reservoir temperature (Ahmad et al., 2016; Moghaddam and Dehagbandi, 2017). Thus, an accurate determination of the MMP for a given oil–gas system is required to ensure a miscible gas enhanced oil recovery project in an oilfield. A number of experimental (Czarnota et al., 2017a, 2017b), theoretical (Hemmati-Sararaddeh et al., 2016; Bian et al., 2016), and empirical methods (Lai et al., 2017; Kaydani et al., 2014) have been developed to determine the MMPs of various oil–gas systems. The experimental methods are considered to be accurate but can be time-consuming and expensive (Elsharkawy et al., 1996) so that the theoretical methods become available and appropriate to predict the MMPs in a sufficiently fast and relatively accurate manner. However, most of existing theoretical methods are targeted at the bulk phase predictions and inapplicable/inaccurate for the MMP determinations in nanopores.

The presence of nanopores in tight formation and its effect on liquid phase behaviour
have been introduced in some studies (Dong et al., 2016), but the MMPs have not been thoroughly analyzed. An initial trial for predicting the MMP in nanopores was undertaken by combining the Peng–Robinson equation of state (PR-EOS) (Peng and Robinson, 1976) with multiple-mixing cell (MMC) algorithm (Ahmadi and Johns, 2011). It is found that the reduction of the MMP is almost 0.90 MPa (130 psi) for a light oil–pure CO$_2$ system and up to 3.45 MPa (500 psi) for a light oil–CO$_2$+CH$_4$ system for a pore radius of 4 nm compared with unconfined pores. Moreover, the confinement effect on the MMP is considered to be marginal if the pore radius is 20 nm or higher (Teklu et al., 2014b). Later, another study for the MMP prediction in nanopores was conducted by applying the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) EOS and VIT technique (S. Wang et al., 2016). The PC-SAFT EOS was associated with the parachor model to predict the IFTs in nanopores, based on which the MMP was estimated by extrapolating to zero IFT. The confinement effect on the MMP is found to be significant when pore radius is smaller than 10 nm. A reduction of 23.5% in MMP is obtained if the pore radius is reduced from infinite to 3 nm. In general, the MMP is decreased under the confinement effect, especially at some extremely small pore levels. The MMP reduction is considered to be caused by the effects of capillary pressure and shifts of the critical temperature and pressure (Zarragoicoechea and Kuz, 2004). Overall, few studies have been found to focus on the MMP prediction in nanopores.

In this chapter, a new interfacial thickness-based diminishing interface method (DIM) and a novel nanoscale-extended correlation are developed to determine the MMPs in bulk phase and nanopores, respectively.
5.2 Diminishing Interface Method

In this part, first, a PR-EOS is modified for the VLE calculations in nanopores by considering the effects of capillary pressure and shifts of the critical temperature and pressure, which is also coupled with the parachor model to predict the IFTs. Second, the interfacial thickness between two mutually soluble phases (e.g., light oil and CO\textsubscript{2} phases) is determined by considering the two-way mass transfer, i.e., CO\textsubscript{2} dissolution into the oil phase and light hydrocarbons (HCs)-extraction from the oil phase by CO\textsubscript{2}. Based on the determined interfacial thicknesses, a new technical method, namely, the diminishing interface method (DIM), is proposed and applied to determine the MMPs. Finally, the phase behaviour and MMPs of three liquid–vapour systems, a pure HC system (i.e., \textit{i}C\textsubscript{4}–\textit{n}C\textsubscript{4}–C\textsubscript{8}) (Ahmadi and Johns, 2011) and two live light oil–pure CO\textsubscript{2} systems (i.e., Pembina and Bakken live light oil–pure CO\textsubscript{2} systems) (Teklu et al., 2014b; Zhang, 2016), are predicted by using the modified PR-EOS and new DIM in bulk phase and nanopores, which are subsequently compared with and validated by the literature results.

5.2.1 Experimental

Materials

In Table 5.1, the detailed compositions of a pure HC system and two live light oil–CO\textsubscript{2} systems used in this study are listed. More specifically, a ternary mixture of 4.53 mol.% \textit{n}-C\textsubscript{4}H\textsubscript{10} + 15.47 mol.% \textit{i}-C\textsubscript{4}H\textsubscript{10} + 80.00 mol.% C\textsubscript{8}H\textsubscript{18} (Wang et al., 2014) is used to be the pure HC system and a Pembina (Zhang, 2016) and a Bakken (Teklu et al., 2014b) live light oil together with pure CO\textsubscript{2} are the two live light oil–CO\textsubscript{2} systems in this study. The properties of the pure HC system and the Bakken live oil–CO\textsubscript{2} system were introduced in the literature (Teklu et al., 2014b; Wang et al., 2014). Moreover, a Pembina dead light oil
Table 5.1

Compositions of liquid and vapour phases for a pure hydrocarbon system (i.e., \(nC_4–iC_4–C_8\) system) (Wang et al., 2014) and two light oil–pure CO\(_2\) systems (i.e., Pembina live light oil–pure CO\(_2\) system (Zhang, 2016) and Bakken live light oil–pure CO\(_2\) system (Teklu et al., 2014b)) used in this study.

<table>
<thead>
<tr>
<th>Pure HCs</th>
<th>Component</th>
<th>Pembina oil Component</th>
<th>Bakken oil Component</th>
<th>Solvent</th>
<th>Pure CO(_2) (mol.%)</th>
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<td>(nC_4)</td>
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<td>100.00</td>
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<tr>
<td></td>
<td></td>
<td>(C_2) 10.70</td>
<td>(C_2) 14.89</td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td>(C_3) 10.69</td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td>(C_5–6) 0.54</td>
<td>(C_5–6) 6.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C_7–12) 2.70</td>
<td>(C_7–12) 15.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(iC_4)</td>
<td>15.47</td>
<td>(C_{13–29}) 2.30</td>
<td>(C_{13–21}) 7.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(C_{30+}) 0.62</td>
<td>(C_{22–80}) 3.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_8)</td>
<td>80.00</td>
<td>Feed oil–solvent ratio (by mole) 0.01 : 0.99</td>
<td>Feed oil–solvent ratio (by mole) 0.50 : 0.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
sample was collected from the Pembina oilfield, Cardium formation in Alberta (Canada). The gas chromatography (GC) compositional analysis of the cleaned Pembina dead oil was performed and the detailed results can be found elsewhere (Zhang, 2016). The Pembina live oil with the gas–oil ratio (GOR) of 15:1 sm$^3$/sm$^3$ was reconstituted by saturating the Pembina dead oil sample with the produced HC gas. The actual composition of the produced gas was equal to 66.50 mol.% CH$_4$ + 11.41 mol.% C$_2$H$_6$ + 11.39 mol.% C$_3$H$_8$ + 10.70 mol.% $n$-C$_4$H$_{10}$. In addition, a Pembina dead light oil–pure CO$_2$ system and a Pembina dead light oil–impure CO$_2$ system are used for MMP determinations in bulk phase. The detailed experimental setups and procedures for preparing the Pembina live oil sample and the impure CO$_2$ sample were described elsewhere (Zhang, 2016).

**PVT tests**

A mercury-free pressure–volume–temperature (PVT) system (PVT-0150-100-200-316-155, DBR, Canada) was used to measure the PVT data of the Pembina dead light oil–CO$_2$ system with four different CO$_2$ concentrations at $T_{res} = 53.0^\circ$C (Zhang and Gu, 2015). The measured PVT data are summarized in Table 5.2. The experimental setup and procedure of the PVT tests were described previously (Zhang, 2016). It is found that the experimentally measured saturation pressure, oil density, and oil-swelling factor (SF) increase with CO$_2$ concentration due to the CO$_2$ dissolution. In this work, the measured Pembina oil PVT data were used to tune the modified Peng–Robinson EOS (PR-EOS) for bulk phase calculations. Moreover, the PVT data for the $i$C$_4$–$n$C$_4$–C$_8$ system from the literature (Wang et al., 2014) are summarized and listed in Table 5.3.

**IFT tests**
Table 5.2

Measured (Zhang, 2016) and calculated saturation pressures, oil densities, and oil-swelling factors (SFs) of the Pembina light oil–pure CO₂ systems at the reservoir temperature of \( T_{\text{res}} = 53.0^\circ \text{C} \).

<table>
<thead>
<tr>
<th>Test no.</th>
<th>( x_{\text{CO}_2} )</th>
<th>( P_{\text{sat}}^{\text{m}} ) (MPa)</th>
<th>( P_{\text{sat}}^{\text{c}} ) (MPa)</th>
<th>( \varepsilon_{\rho} ) (%)</th>
<th>( \rho_{\text{oil}}^{\text{m}} ) (g/cm(^3))</th>
<th>( \rho_{\text{oil}}^{\text{c}} ) (g/cm(^3))</th>
<th>( \varepsilon_{\rho} ) (%)</th>
<th>( SF_{\text{m}}^{\text{at} P_{\text{sat}}} )</th>
<th>( SF_{\text{c}}^{\text{at} P_{\text{sat}}} )</th>
<th>( \varepsilon_{SF} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.8300</td>
<td>0.8311</td>
<td>0.13</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>10.40</td>
<td>35.90</td>
<td>6.50</td>
<td>6.52</td>
<td>0.31</td>
<td>0.8432</td>
<td>0.8439</td>
<td>0.08</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>3</td>
<td>13.40</td>
<td>42.70</td>
<td>7.80</td>
<td>7.77</td>
<td>0.38</td>
<td>0.8440</td>
<td>0.8446</td>
<td>0.07</td>
<td>1.20</td>
<td>1.19</td>
</tr>
<tr>
<td>4</td>
<td>18.20</td>
<td>51.70</td>
<td>9.60</td>
<td>9.63</td>
<td>0.31</td>
<td>0.8485</td>
<td>0.8488</td>
<td>0.04</td>
<td>1.28</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Notes:
- \( x_{\text{CO}_2} \): weight or mole percentage of CO₂ dissolved into the dead light oil
- \( P_{\text{sat}}^{\text{m}} \): measured saturation pressure
- \( P_{\text{sat}}^{\text{c}} \): calculated saturation pressure
- \( \rho_{\text{oil}}^{\text{m}} \): measured oil density
- \( \rho_{\text{oil}}^{\text{c}} \): calculated oil density
- \( SF_{\text{m}} \): measured oil-swelling factor
- \( SF_{\text{c}} \): calculated oil-swelling factor
- \( \varepsilon \): relative error between the calculated and measured data
Table 5.3

Measured (Wang et al., 2014) and calculated pressure–volume–temperature data for iC4–nC4–C8 system in the micro-channel of 10 µm and nano-channel of 100 nm at (a) constant pressure and (b) constant temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before flash calculation</th>
<th>After flash calculation (this study)</th>
<th>After flash calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>24.9</td>
<td>85,260</td>
<td>71.9</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid (iC4–nC4–C8, mol.%)</td>
<td>15.47 4.53 80.00 4.88</td>
<td>1.87 93.25 5.09 1.68 93.23</td>
<td></td>
</tr>
<tr>
<td>Vapour (iC4–nC4–C8, mol.%)</td>
<td>0 0 0 64.35</td>
<td>16.82 18.83 62.84 17.56 19.60</td>
<td></td>
</tr>
<tr>
<td>Liquid fraction (mol.%)</td>
<td>100.00</td>
<td>82.20</td>
<td>82.03</td>
</tr>
<tr>
<td>Vapour fraction (mol.%)</td>
<td>0.00</td>
<td>17.80</td>
<td>17.97</td>
</tr>
<tr>
<td>IFT (mJ/m²)</td>
<td>–</td>
<td>16.24</td>
<td>15.68</td>
</tr>
<tr>
<td>P_{cap} in micro-channel (kPa)</td>
<td>–</td>
<td>3.38</td>
<td>1.92</td>
</tr>
<tr>
<td>P_{cap} in nano-channel (kPa)</td>
<td>–</td>
<td>286.91</td>
<td>185.63</td>
</tr>
</tbody>
</table>

| Temperature (°C)                                | 71.9                     |                                     |                        |
| Pressure (Pa)                                   | 839,925                  | 426,300                             |                        |
| Liquid (iC4–nC4–C8, mol.%)                      | 61.89 18.11 20.00 28.59   | 11.15 60.26 18.98 6.44 74.58       |                        |
| Vapour (iC4–nC4–C8, mol.%)                      | 0 0 0 75.82              | 21.01 3.16 76.66 19.35 3.99        |                        |
| Liquid fraction (mol.%)                         | 100.00                   | 29.50                               | 30.38                  |
| Vapour fraction (mol.%)                         | 0.00                     | 70.50                               | 69.62                  |
| IFT (mJ/m²)                                     | –                        | 13.33                               | 12.89                  |
| P_{cap} in micro-channel (kPa)                  | –                        | 2.77                                | 1.88                   |
| P_{cap} in nano-channel (kPa)                   | –                        | 235.54                              | 182.49                 |
The IFTs between the Pembina light oil and CO$_2$ are measured by applying the ADSA technique for the pendant drop case, which was described in detail elsewhere (Gu et al., 2013). The high-pressure IFT cell (IFT-10, Temco, USA) is rated to 69.0 MPa and 177.0°C. The IFT-cell volume is 49.5 cm$^3$. The ADSA program requires the density difference between the oil drop and the CO$_2$ phase at the test conditions and the local gravitational acceleration as the input data. The dead/live oil sample densities at different test conditions were measured experimentally by using a densitometer (DMA512P, Anton Paar, USA). The CO$_2$ density was predicted by using the CMG WinProp module (Version 2016.10, Computer Modelling Group Limited, Canada) under the same test conditions. Three respective series of the IFT tests for the Pembina dead light oil–pure CO$_2$ system, live light oil–pure CO$_2$ system, and dead light oil–impure CO$_2$ system were conducted at $T_{res} = 53.0^\circ$C (Gu et al., 2013; Zhang, 2016). The detailed experimental data of these three series of the IFT tests are listed in Table 5.4.

5.2.2 Theory

**Modified equation of state**

In this study, a modified PR-EOS is proposed to calculate the VLE properties in nanopores (Brusilovsky, 1992). More specifically, first, the PR-EOS (Peng and Robinson, 1976) is shown as follows:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)}$$

where

$$a = \frac{0.45724 R^2 T^2}{P_c} \text{e}^{-\alpha(T)}$$

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Table 5.4

Measured (Zhang and Gu, 2016b) and calculated twelve interfacial tensions (IFTs) at twelve different pressures and the reservoir temperature of $T_{res} = 53.0^\circ \text{C}$ for the Pembina dead light oil–pure $\text{CO}_2$ system, live light oil–pure $\text{CO}_2$ system, and dead light oil–impure $\text{CO}_2$ system, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Pembina dead light oil–pure $\text{CO}_2$ system</th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$ (MPa)</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
<td>5.5</td>
<td>6.5</td>
<td>7.5</td>
<td>8.5</td>
<td>9.5</td>
<td>10.0</td>
<td>12.0</td>
<td>15.0</td>
</tr>
<tr>
<td>$\gamma^m$ (mJ/m²)</td>
<td>16.89</td>
<td>15.50</td>
<td>14.02</td>
<td>11.57</td>
<td>10.02</td>
<td>7.39</td>
<td>5.01</td>
<td>3.74</td>
<td>3.00</td>
<td>2.05</td>
<td>1.45</td>
</tr>
<tr>
<td>$\gamma^c$ (mJ/m²)</td>
<td>16.58</td>
<td>14.92</td>
<td>13.36</td>
<td>10.77</td>
<td>9.01</td>
<td>7.00</td>
<td>5.13</td>
<td>3.31</td>
<td>2.43</td>
<td>1.49</td>
<td>1.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pembina live light oil–pure $\text{CO}_2$ system</th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>$P$ (MPa)</td>
<td>1.8</td>
<td>3.0</td>
<td>3.8</td>
<td>4.8</td>
<td>5.6</td>
<td>7.0</td>
<td>8.6</td>
<td>10.1</td>
<td>11.4</td>
<td>15.0</td>
<td>16.6</td>
<td>18.1</td>
</tr>
<tr>
<td>$\gamma^m$ (mJ/m²)</td>
<td>17.77</td>
<td>15.24</td>
<td>13.79</td>
<td>12.67</td>
<td>10.81</td>
<td>8.75</td>
<td>5.89</td>
<td>4.34</td>
<td>4.04</td>
<td>3.28</td>
<td>2.56</td>
<td>1.75</td>
</tr>
<tr>
<td>$\gamma^c$ (mJ/m²)</td>
<td>17.17</td>
<td>15.21</td>
<td>13.96</td>
<td>12.42</td>
<td>11.07</td>
<td>8.76</td>
<td>6.22</td>
<td>4.15</td>
<td>2.97</td>
<td>1.94</td>
<td>1.35</td>
<td>0.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Pembina dead light oil–impure $\text{CO}_2$ system</th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$ (MPa)</td>
<td>2.0</td>
<td>3.0</td>
<td>4.5</td>
<td>6.0</td>
<td>7.0</td>
<td>8.5</td>
<td>10.0</td>
<td>12.5</td>
<td>15.0</td>
<td>19.0</td>
<td>21.0</td>
<td>24.0</td>
</tr>
<tr>
<td>$\gamma^m$ (mJ/m²)</td>
<td>17.56</td>
<td>15.99</td>
<td>13.93</td>
<td>11.58</td>
<td>9.69</td>
<td>7.82</td>
<td>5.95</td>
<td>4.11</td>
<td>3.01</td>
<td>2.05</td>
<td>1.88</td>
<td>1.34</td>
</tr>
<tr>
<td>$\gamma^c$ (mJ/m²)</td>
<td>16.79</td>
<td>15.41</td>
<td>13.11</td>
<td>10.88</td>
<td>9.46</td>
<td>7.50</td>
<td>5.76</td>
<td>3.22</td>
<td>2.33</td>
<td>1.02</td>
<td>0.88</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Notes:  
$m$: Measured IFTs  
c: calculated IFTs
\[ b = \frac{0.0778RT_c}{P_c} \]

\[ \alpha(T) = [1 + m(1 - \sqrt{T_c})]^2 \]

\[ m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \]

where \( P \) is the system pressure; \( R \) is the universal gas constant; \( T \) is the temperature; \( a \) and \( b \) are EOS constants; \( \nu \) is the molar volume; \( T_c \) is the critical temperature in bulk phase; \( P_c \) is the critical pressure in bulk phase; \( T_r \) is the reduced temperature; and \( \omega \) is the acentric factor.

The shifts of critical properties (i.e., critical temperature and pressure) of the confined fluids are considered to occur in nanopores, which is specifically studied in the previous study (Zarragoicoechea and Kuz, 2004) and related with the ratio of the Lennard-Jones size diameter \( \left( \sigma_{LJ} \right) \) and the pore radius as follows,

\[ T_{cp} = T_c - T_c [0.9409 \frac{\sigma_{LJ}}{r_p} - 0.2415 \left( \frac{\sigma_{LJ}}{r_p} \right)^2] \quad (5.2) \]

\[ P_{cp} = P_c - P_c [0.9409 \frac{\sigma_{LJ}}{r_p} - 0.2415 \left( \frac{\sigma_{LJ}}{r_p} \right)^2] \quad (5.3) \]

where \( \sigma_{LJ} = 0.244 \frac{T_c}{\sqrt{P_c}} \); \( T_{cp} \) is the critical temperature in nanopores; \( P_{cp} \) is the critical pressure in nanopores; \( r_p \) is the pore radius.

The initial \( K \)-value of each component can be estimated from Wilson’s equation (Wilson, 1964),

\[ K_i = \frac{P_{ci}}{P} \exp[5.37(1 + \omega)(1 - \frac{T_{ci}}{T})] \quad (5.4) \]

where \( P_{ci} \) is the critical pressure of component \( i \); \( T_{ci} \) is the critical temperature of
component $i$; $\omega_i$ is the acentric factor of component $i$. Then the Rachford–Rice equation is applied to calculate $x_i$ and $y_i$,

$$\sum_{i=1}^{N} \frac{z_i(K_i - 1)}{1 + (K_i - 1)\beta} = 0$$

(5.5)

where $\beta$ is the vapour fraction.

The compressibility of the liquid or vapour phase can be determined,

$$Z_L^3 - (1 - B_L)Z_L^2 + (A_L - 3B_L^2 - 2B_L)Z_L - (A_LB_L - B_L^2 - B_L^3) = 0$$

(5.6a)

$$Z_V^3 - (1 - B_V)Z_V^2 + (A_V - 3B_V^2 - 2B_V)Z_V - (A_VB_V - B_V^2 - B_V^3) = 0$$

(5.6b)

where $Z_L$ and $Z_V$ are the respective compressibility factors of the liquid and vapour phases;

$$A_L = \frac{aP_L}{R^2T^2}, \quad B_L = \frac{bP_L}{RT}, \quad A_V = \frac{aP_V}{R^2T^2}, \quad B_V = \frac{bP_V}{RT}.$$  Constants of $a$ and $b$ are obtained by applying the van der Waals mixing rule,

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

(5.7a)

$$b = \sum_i x_i b_i$$

(5.7b)

where $a_{ij}$ is the binary interaction of component $i$ and component $j$, $a_{ij} = (1 - k_{ij})\sqrt{a_i a_j}$; $k_{ij}$ is the binary interaction coefficient of component $i$ and component $j$; $k_{ii} = k_{jj} = 0$. Minimum Gibbs free energy is applied to select roots of the compressibility factors for the liquid and vapour phases (Whitson and Brule, 2000).

The liquid and vapour phases are assumed to be the wetting phase and non-wetting phase, respectively (Nojabaei et al., 2013). Thus the capillary pressure ($P_{cap}$) is,

$$P_{cap} = P_V - P_L$$

(5.8)
where $P_v$ is the pressure of the vapour phase and $P_L$ is the pressure of the liquid phase.

On the other hand, the capillary pressure can be expressed by Young–Laplace equation,

$$P_{cap} = \frac{2\gamma}{r_p} \cos \theta \quad (5.9)$$

where $\gamma$ is the interfacial tension and $\theta$ is the contact angle of the vapour–liquid interface with respect to the pore surface, which is assumed to be 30° according to the experimental results in the literature (Wang et al., 2014). Therein, the IFT is estimated by means of the Macleod–Sugden equation, which will be specifically introduced later.

The fugacity coefficient of a mixture is,

$$\ln \phi_i^L = \left( \frac{b_i}{b} \right)_L (Z_L - 1) - \ln(Z_L - B_L) - \frac{A_L}{2\sqrt{2}B_L} \left[ 2 \left( \frac{a_i}{a} \right)_{L_{0.5}} - \left( \frac{b_i}{b} \right)_L \right] \ln\left( \frac{Z_L + (1 + \sqrt{2})B_L}{Z_L + (1 - \sqrt{2})B_L} \right)$$

$$\ln \phi_i^V = \left( \frac{b_i}{b} \right)_V (Z_V - 1) - \ln(Z_V - B_V) - \frac{A_V}{2\sqrt{2}B_V} \left[ 2 \left( \frac{a_i}{a} \right)_{V_{0.5}} - \left( \frac{b_i}{b} \right)_V \right] \ln\left( \frac{Z_V + (1 + \sqrt{2})B_V}{Z_V + (1 - \sqrt{2})B_V} \right) \quad (5.10a)$$

The VLE calculations based on the modified PR-EOS require a series of iterative computation through, for example, the Newton–Raphson method. Figure 5.1 shows the flowchart of the VLE calculation process. The detailed IFT calculations have been aforementioned.

**Derivation of interfacial thickness**
Figure 5.1 Flowchart of the modified Peng–Robinson equation of state for phase property predictions and parachor model for interfacial tension calculations in nanopores.
In this study, a formula for determining the interfacial thickness between two mutually soluble phases (e.g., oil and CO\textsubscript{2} phases) is derived by taking account of the two-way mass transfer. Suppose that a closed system, as shown in Figure 5.2, consists of two mutually soluble phases (\(\alpha\) and \(\beta\)), each of which has two components (1 and 2), the Gibbs free energy as an interfacial excess quantity is given by (Guggenheim, 1985),

\[
G(p, T) = \gamma A + \mu_1 N_1 + \mu_2 N_2 = U + PV - TS
\]  

(5.11)

where \(A\) is the surface area of the interface, \(\mu\) is the chemical potential, \(N_j\) is the mole number of the \(j^{th}\) component, \(U\) is the internal energy, \(V\) is the volume, \(S\) is the entropy. Two-way mass transfer occurs so that there is not only internal energy (\(U\)) change but also external potential energy (\(Y\)) change,

\[
(U^\alpha + Y^\alpha) + (U^\beta + Y^\beta) = TS - PV + \gamma A + (\mu^\alpha_1 N_1 + \mu^\beta_1 N_1 + \mu^\beta_2 N_2 + \mu^\alpha_2 N_2^\alpha)
\]  

(5.12)

Legendre transforms of the internal energy plus external potential energy gives,

\[
d[(U^\alpha + Y^\alpha) + (U^\beta + Y^\beta)] = T dS - P dV + \gamma dA + (\mu^\alpha_1 dN_1 + \mu^\beta_1 dN_1 + \mu^\beta_2 dN_2 + \mu^\alpha_2 dN_2^\alpha)
\]  

(5.13)

Given the fact that \((N_1^\alpha + N_1^\beta)\) and \((N_2^\alpha + N_2^\beta)\) are constant because of mass conservation, Eq. (5.13) is rewritten as,

\[
d[(U^\alpha + Y^\alpha) + (U^\beta + Y^\beta)] = T dS - P dV + \gamma dA + (\mu^\alpha_1 - \mu^\beta_1) dN_1^\alpha + (\mu^\beta_2 - \mu^\alpha_2) dN_2^\beta
\]  

(5.14)

In Eq. (5.14), \([\mu^\alpha_i - \mu^\beta_i] dN_1^\alpha + (\mu^\beta_2 - \mu^\alpha_2) dN_2^\beta\] is referred to as the chemical potential changes due to the interfacial mass transfer. Physically, \([\mu^\alpha_i - \mu^\beta_i] dN_1^\alpha\] or \([\mu^\beta_2 - \mu^\alpha_2] dN_2^\beta\] represents the change of the internal energy and external potential
Figure 5.2 Schematic diagram of the interfacial structure between two miscible phases: (a) real case and; (b) ideal case.
energy for each component.

Then, subtracting differentiation of \((\gamma A + \mu_1 N_1 + \mu_2 N_2)\) from the full differentiation of \([(U + Y) + PV - TS]\) yields,

\[
-SdT + VdP - N_1 d\mu_1 - N_2 d\mu_2 = Ad\gamma
\]

The Gibbs-Duhem equation for each phase can be written (Lyklema, 1991),

\[
-S^\alpha dT + V^\alpha dP^\alpha + N_1^\alpha d\mu_1 + N_2^\alpha d\mu_2 = 0 \quad \text{Phase } \alpha \tag{5.16a}
\]

\[
-S^\beta dT + V^\beta dP^\beta + N_1^\beta d\mu_1 + N_2^\beta d\mu_2 = 0 \quad \text{Phase } \beta \tag{5.16b}
\]

Two undetermined Lagrange multipliers, \(\lambda^\alpha\) and \(\lambda^\beta\), are introduced and applied into Eqs. (5.16a) and (5.16b). Afterwards, Eq. (5.15) is used to subtract them, which is then divided by interfacial area \(A\),

\[
d\gamma = \left(\frac{-(S - \lambda^\alpha S^\alpha - \lambda^\beta S^\beta)}{A} dT + \frac{(V - \lambda^\alpha V^\alpha - \lambda^\beta V^\beta)}{A} dP - \frac{(N_1 - \lambda^\alpha N_1^\alpha - \lambda^\beta N_1^\beta)}{A} d\mu_1 - \frac{(N_2 - \lambda^\alpha N_2^\alpha - \lambda^\beta N_2^\beta)}{A} d\mu_2\right)
\]

Let,

\[
\bar{S} = \left(S - \lambda^\alpha S^\alpha - \lambda^\beta S^\beta\right)/A \tag{5.18a}
\]

\[
\bar{\delta} = (V - \lambda^\alpha V^\alpha - \lambda^\beta V^\beta)/A \tag{5.18b}
\]

\[
\Gamma_1 = (N_1 - \lambda^\alpha N_1^\alpha - \lambda^\beta N_1^\beta)/A \tag{5.18c}
\]

\[
\Gamma_2 = (N_2 - \lambda^\alpha N_2^\alpha - \lambda^\beta N_2^\beta)/A \tag{5.18d}
\]

Then, Eq. (5.17) can be represented as,

\[
d\gamma = -\bar{S}dT + \bar{\delta}dP - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{5.19}
\]

Theoretically, two Lagrange multipliers \(\lambda^\alpha\) and \(\lambda^\beta\) could be determined by setting any two
of the interfacial excess quantities (i.e., \(\pi, \delta, \Gamma_1, \Gamma_2\)) to be zero, the choices of which are purely conventional (Yang and Li, 1996). At a given \(P\) and \(T\), the chemical potentials cannot be determined and should be eliminated as independent variables so that \(\Gamma_1\) and \(\Gamma_2\) are set to be zero,

\[
d\gamma = -\delta dT + \partial dP
\]  
(5.20)

\(T\) remains constant in the study, i.e., \(dT = 0\), so,

\[
\delta = (\frac{\partial \gamma}{\partial P})_T
\]  
(5.21)

In Eq. (5.21), \(\delta\) is the distance between two miscible phases, which is also denoted as the interfacial thickness.

In addition to the above derivations, there is another series of derivations for the interfacial thickness based on the Gibbs convention is proposed. First, dividing Eqs. (5.16a) and (5.16b) by volume \(V^\alpha\) and \(V^\beta\) at the constant temperature,

\[
-dP^\alpha = n_1^\alpha d\mu_1 + n_2^\alpha d\mu_2 \quad \text{Phase } \alpha
\]  
(5.22a)

\[
-dP^\beta = n_2^\beta d\mu_2 + n_1^\beta d\mu_1 \quad \text{Phase } \beta
\]  
(5.22b)

where \(n_1^\alpha\) and \(n_1^\beta\) are the molar concentrations of the first component in \(\alpha\) and \(\beta\) phases, respectively; \(n_2^\alpha\) and \(n_2^\beta\) are the molar concentrations of the second component in \(\alpha\) and \(\beta\) phases, respectively.

Gibbs convention at a constant temperature states (Gibbs, 1961),

\[
-(\frac{\partial \gamma}{\partial P})_T = \sum_{i=1}^{i} \Gamma_i (\frac{\partial \mu_i}{\partial P})_T
\]  
(5.23)

Assuming the location of \(\Gamma_1 = 0\) to be the reference surface,

\[
N_1 = z_1 n_1^\beta + (H - z_1) n_1^\alpha
\]  
(5.24)
where \(z_1\) is the surface location and \(H\) is the total height. For Component 1, with respect to the surface at \(z_2\) and a random location \(b\),

\[N_1 = z_2 n_1^\beta + (H - z_2) n_1^\alpha + \Gamma_1^{(z_2)} = b n_1^\beta + (H - b) n_1^\alpha + \Gamma_1^{(b)} \text{ (5.25)}\]

Similar equations can be obtained for substance 2.

Eqs. (5.24) and (5.25) are subtracted to obtain \(\Gamma_1^{(b)} = \delta(n_1^\alpha - n_1^\beta)\). Similarly, \(\Gamma_2^{(b)} = \delta(n_2^\alpha - n_2^\beta)\). Given the assumption of \(P^\alpha = P^\beta = P\), Eqs. (5.22a) and (5.22b) are rearranged to be,

\[
\frac{\partial \mu_1}{\partial P} = \frac{n_2^\alpha - n_2^\beta}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \text{ (5.26a)} \\
\frac{\partial \mu_2}{\partial P} = \frac{n_1^\beta - n_1^\alpha}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \text{ (5.26b)}
\]

Then, Eqs. (5.26a) and (5.26b) are combined into Eq. (5.23),

\[
\frac{\partial \gamma}{\partial P} = -\frac{1}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \left( \frac{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \right) \text{ (5.27a)}
\]

\[
\frac{\partial \gamma}{\partial P} = -\frac{1}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \left( \frac{n_1^\beta - n_1^\alpha}{n_1^\beta - n_1^\alpha} \right) \text{ (5.27b)}
\]

Since \(\delta = \frac{\Gamma_i^b - \Gamma_i^d}{\Delta n_i}\), \(b\) or \(d\) means any location in the system. Thus the interfacial thickness is,

\[
\delta = -\left( \frac{1}{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta} \right) \left[ \frac{n_1^\alpha n_2^\beta - n_2^\alpha n_1^\beta}{(n_1^\beta - n_1^\alpha)(n_2^\alpha - n_2^\beta)} \right] \text{ (5.28)}
\]

In this study, phase \(\alpha\) is the vapour phase, phase \(\beta\) is the liquid phase, substance 1 is
CO₂, and substance 2 is oil. For a light oil–CO₂ system, 
\[ \frac{n_{\text{CO}_2} V_{\text{oil}} - n_{\text{CO}_2} L_{\text{oil}}}{(n_{\text{CO}_2} V_{\text{oil}} - n_{\text{CO}_2} L_{\text{oil}})} \approx -1. \]

Thus Eq. (5.28) is simplified to be \( \delta = \left. \frac{\partial \gamma}{\partial P} \right|_T \), which represents the interfacial thickness between two mutually soluble phases as defined in Eq. (5.24).

It should be noted that the sign of \( \delta \) is determined by the characteristics of the two bulk phases. More specifically, if the two phases are barely mutually soluble and repulsive intermolecular interaction dominates in the interfacial region, \( \delta > 0 \). If the two phases are mutually soluble and two-way mass transfer occurs across the interface, \( \delta < 0 \). In this study, the interfacial tension of the light oil–CO₂ system is decreased with the pressure so that \( \delta \) is negative. Although the sign of \( \delta \) can be positive, zero, or negative, the physical interfacial thickness has to be positive (Yang and Li, 1996).

### 5.2.4 Results and discussion

**Phase behaviour in bulk phase and nanopores**

The bulk phase PVT tests with four different CO₂ concentrations of 0.00, 35.90, 42.70, and 51.70 mol.% in the Pembina light oil were conducted at the reservoir temperature of \( T_{\text{res}} = 53.0°C \) and are summarized in Table 5.2. It is found that the measured saturation pressure, oil density, and oil-swelling factor (SF) increase with CO₂ concentration. The modified PR-EOS was tuned by using a set of major tuning parameters (Agarwal et al., 1987; Jindrová et al., 2015). More specifically, the binary interaction coefficient (BIC) between CO₂ and C₃₀₊, critical pressure and temperature, and acentric factor of C₃₀₊ were adjusted to match the measured PVT data. The final predicted saturation pressures, oil densities, and oil-swelling factors are compared with the measured PVT data in Table 5.2.
The predicted data are found to agree well with the measured PVT data since their relative errors are rather small. It should be noted that the above-mentioned tuning parameters are adjusted for one time and applied to predict the phase behaviour of the three liquid–vapour systems in this study.

In micro- and nano-channels, the vapour and liquid compositions before and after flash calculations for the \textit{iC}_4–\textit{nC}_4–\textit{C}_8 system at two different conditions (i.e., constant pressure and constant temperature) are obtained from literature (Wang et al., 2014) and summarized in Tables 5.3a and b. Some detailed analyses can be found in the previous study (Wang et al., 2014). More importantly, it is found that the lighter components (i.e., \textit{iC}_4 and \textit{nC}_4) prefer to be in the vapour phase by increasing the temperature or decreasing the pressure. The predicted compositions and fractions of the liquid and vapour phases as well as IFTs are listed in Tables 5.3a and 3b, which agree well with the literature results. The predicted capillary pressure either in micro-channel (10 \( \mu \)m) or nano-channel (100 nm) is slightly lower than the literature data for both cases. In a similar manner with the literature, the predicted capillary pressure in the nano-channel is almost two orders of magnitude higher than that in the micro-channel. Besides, the modified PR-EOS is also applied to calculate the bubble-point and dew-point pressures of the Bakken live light oil–pure \textit{CO}_2 system at pore radius of 10 and 3 nm, which are also in a good agreement with the literature figure (Teklu et al., 2014b). The comparison figure cannot be presented because no precise data but a figure was given in the literature. Overall, the modified PR-EOS in this study is capable of predicting the phase behaviour of the pure HC system and/or light oil–\textit{CO}_2 systems in bulk phase and/or nanopores, whose results agree well with the literature data.

**In bulk phase**

In this study, the measured (Gu et al., 2013; Zhang and Gu, 2016b) and predicted IFTs
**Figure 5.3a** Determined minimum miscibility pressures of the Pembina dead light oil–pure CO₂ system from the diminishing interface method (DIM) at $T_{res} = 53.0°C$. 
Figure 5.3b Determined minimum miscibility pressures of the Pembina live light oil–pure CO₂ system from the diminishing interface method (DIM) at $T_{res} = 53.0°C$. 
Figure 5.3c Determined minimum miscibility pressures of the Pembina dead light oil–impure CO$_2$ system from the diminishing interface method (DIM) at $T_{res} = 53.0^\circ$C.
are plotted in Figures 5.3a–c for the Pembina dead light oil–pure CO$_2$ system, live light oil–pure CO$_2$ system, and dead light oil–impure CO$_2$ system at different pressures and $T_{res} = 53.0^\circ$C, respectively. The measured and predicted IFTs match well especially at lower pressures, both of which are quickly reduced with the pressure. When the pressure is higher than 10 MPa, the predicted IFT is lower than the measured IFT. In the IFT tests, the pendant oil drop that was formed eventually is mainly consisted of relatively heavy paraffinic (i.e., HCs), aromatic, or asphalitic components of the original dead light oil after the initial quick and subsequent slow HCs-extractions by CO$_2$ at a higher pressure (Zhang et al., 2018e). Thus the measured IFT at a higher pressure is between the remaining oil phase and the CO$_2$ phase with some extracted light to intermediate HCs. In the EOS modeling, however, the light oil is characterized and represented by using a series of alkanes (i.e., C$_3$–C$_{30+}$) rather than a combination of the paraffinic, aromatic, or asphalitic molecules. The predicted IFT is between the intermediate to heavy alkanes of the light oil and the CO$_2$ phase with some extracted light to intermediate alkanes at a higher pressure. This is why the predicted IFT is slightly lower than the measured IFT at a higher pressure. Overall, the modified PR-EOS coupled with the parachor model is proven to be able to accurately predict the IFTs in bulk phase.

In theoretical section, the interfacial thickness ($\delta$) is defined as the partial derivative of the IFT ($\gamma$) with respect to the pressure ($P$) at a constant temperature, i.e., $\delta = (\partial \gamma / \partial P)_T$. In this study, the interfacial thickness is obtained by using the forward finite difference approximation (FDA) of the partial derivative of the IFT ($\gamma$) with respect to the pressure ($P$) at a constant temperature, i.e., $\delta = (\Delta \gamma / \Delta P)_T$. The IFTs and interfacial thicknesses between the bulk oil and CO$_2$ phases as well as the FDA of the partial derivative
of the interfacial thickness (second derivative of the IFT) with respect to the pressure at a constant temperature, i.e., \((\Delta \delta / \Delta P)_T\), for the three Pembina light oil–CO_2 systems are plotted in Figures 5.3a–c. It is found that the IFT of the each light oil–CO_2 system is reduced with the pressure since the dead/live light oil and pure/impure CO_2 phase are mutually soluble. Thus the sign of \(\delta\) is negative in this study. However, it should be noted the physical interfacial thickness is always positive even if the sign of \(\delta\) could be positive, zero, or negative (Yang and Li, 1996).

It is seen from Figures 5.3a–c that the interfacial thicknesses of the three Pembina light oil–CO_2 systems are different, but overall, they are decreased with the pressure. More specifically, the interfacial thickness of the Pembina dead light oil–pure CO_2 system is slightly increased initially, then it is quickly decreased and finally tends to be stabilized. It is slightly different in the Pembina live light oil–pure CO_2 system that the interfacial thickness is level off at the initial stage. However, the interfacial thickness of the dead light oil–impure CO_2 system is continuously decreased with the pressure. It is worthwhile to mention that among the three systems, the interfacial thickness of the dead light oil–pure CO_2 system is quickly reduced to be the minimum at a high pressure while that of the dead light oil–impure CO_2 system is decreased slowly and tends to be the largest at a high pressure. Furthermore, the inflection point of the derivative of the interfacial thickness with respect to the pressure \((\Delta \delta / \Delta P)_T\) vs. pressure curve is found to be in a good agreement with \(P^A\) for each Pembina light oil–CO_2 system.

In terms of the DIM, the MMP is determined by linearly regressing and extrapolating the derivative of the interfacial thickness with respect to the pressure \((\Delta \delta / \Delta P)_T\) vs.
pressure data to zero. Physically, \((\Delta\delta/\Delta P)_r = 0\) means the interfacial thickness between the oil and CO\(_2\) phases becomes constant and does not change with the pressure. Thus it is inferred that a stable interfacial thickness between the oil and CO\(_2\) phases rather than a conventional zero-IFT condition is obtained when the miscibility is achieved.

Mathematically, the linearity of such a linear regression can be represented by the so-called linear correlation coefficient (LCC) or \(R^2\). More specifically, the LCC of the linear regression of the data points from the highest \((\Delta\delta/\Delta P)_r\) point at the lowest pressure to any point at an arbitrarily higher pressure is obtained for the MMP determination. In the previous study (Zhang and Gu, 2016b), \(R^2_c = 0.990\) is considered to be a critical value of the LCC criterion. Hence, in this study, the MMPs of the Pembina dead light oil–pure CO\(_2\) system, live light oil–pure CO\(_2\) system, and dead light oil–impure CO\(_2\) system are determined to be 12.4, 15.0, and 22.1 MPa by using the LCC criterion from the DIM at \(T_{res} = 53.0^\circ\)C and shown in Figures 5.3a–c.

It is seen from Table 5.5 that the determined MMPs from the DIM for the Pembina dead and live light oil–pure CO\(_2\) systems agree well with 12.4–12.9 MPa from the coreflood tests and 15.2–15.4 MPa from the slim-tube tests (Zhang and Gu, 2015). In the Pembina dead light oil–impure CO\(_2\) system, the determined MMP from the DIM is slightly lower than that from the RBA tests but similar to that from the VIT technique. It is inferred that the determined MMP may be overestimated by means of the RBA tests (Zhang and Gu, 2016a). As mentioned above, \(P^B\) is determined to be 13, 15, and 23 MPa by using the 1 mol.%/MPa criterion, at which the two-phase compositional change is considered to reach its maximum. It is found that the determined MMPs of the three light oil–CO\(_2\)
Table 5.5

Determined minimum miscibility pressures (MMPs) of the Pembina dead light oil–pure CO₂ system, live light oil–pure CO₂ system, and dead light oil–impure CO₂ system in bulk phase from the vanishing interfacial tension (VIT) technique, coreflood tests, slim-tube tests, rising-bubble apparatus (RBA) tests, and diminishing interface method (DIM) at the reservoir temperature of $T_{\text{res}} = 53.0^\circ \text{C}$.

<table>
<thead>
<tr>
<th>Test system</th>
<th>VIT-MMP (MPa)</th>
<th>Coreflood tests MMP (MPa)</th>
<th>Slim-tube tests MMP (MPa)</th>
<th>RBA-MMP (MPa)</th>
<th>DIM-MMP (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Traditional</td>
<td>Improved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pembina dead light oil–pure CO₂</td>
<td>10.6</td>
<td>12.9</td>
<td>12.4–12.9</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pembina live light oil–pure CO₂</td>
<td>12.5</td>
<td>13.2</td>
<td>–</td>
<td>15.2–15.4</td>
<td>–</td>
</tr>
<tr>
<td>Pembina dead light oil–impure CO₂</td>
<td>21.4</td>
<td>21.8</td>
<td>–</td>
<td>–</td>
<td>23.4–23.5</td>
</tr>
<tr>
<td>Reference</td>
<td>(40)</td>
<td>(18)</td>
<td>(9)</td>
<td>(9)</td>
<td>(54)</td>
</tr>
</tbody>
</table>
systems from the DIM in Figures 5.3a–c are in good agreement with $p^B$ in Figures 4.2a–c. Thus the DIM is concluded to be physically meaningful for determining the MMP since the two-phase compositional change is found to reach the maximum at the determined MMP from the DIM. In summary, the DIM is proven to be accurate and in a physically meaningful way for determining the MMPs in bulk phase.

**In nanopores**

The modified PR-EOS coupled with the parachor model is applied to predict the IFTs of the Bakken live light oil–pure $\text{CO}_2$ system at different pressures and $T_{res} = 116.1^\circ\text{C}$ in nanopores, which are summarized, plotted and compared with the predicted data from the literature (Teklu et al., 2014b) in Figure 5.4a. The predicted IFTs in this study agree well with the recorded IFTs from the literature, both of which always decrease with pressure increases. At a constant pressure, it is found that the confinement effect is negligible and the predicted IFTs remain almost unchanged when the pore radius is larger than 100 nm. Once the pore radius is smaller than 100 nm, the predicted IFT is decreased with a reduction of pore radius. This is because the pressure of the vapour phase is increased with the addition of the capillary pressure (note that the vapour phase is assumed to be the non-wetting phase), which leads the density of the vapour phase (i.e., second term of the Macleod–Sugden equation) to increase. That is why the predicted IFTs from the parachor model become smaller with a reduction of pore radius/an increase of confinement effect. The predicted IFTs at a lower pressure are also found to decrease more significantly by reducing the pore radius when compared with those at a higher pressure. In a similar manner with the Bakken live light oil–pure $\text{CO}_2$ system, the predicted IFTs of the Pembina live light oil–pure $\text{CO}_2$ system in the pore radius range of 2 to 1,000,000 nm at three
Figure 5.4a Confinement effect on predicted interfacial tensions of the Bakken live light oil–pure CO$_2$ system from the literature (Teklu et al., 2014b) and the model in this study in the pore radius range of 4–1,000 nm at four different pressures and $T_{res} = 116.1^\circ$C.
Figure 5.4 Confinement effect on predicted interfacial tensions of the Pembina live light oil–pure CO$_2$ system from the model in this study in the pore radius range of 2–1,000,000 nm at three different pressures and $T_{res} = 53.0^\circ$C.
Determined minimum miscibility pressures of Pembina live light oil–pure CO\textsubscript{2} system in the nanopores of 100 nm at $T_{\text{res}} = 53.0^\circ\text{C}$.

**Figure 5.5a**
Figure 5.5b Determined minimum miscibility pressures of Pembina live light oil–pure CO₂ system in the nanopores of 20 nm at $T_{res} = 53.0^\circ C$. 
Figure 5.5c Determined minimum miscibility pressures of Pembina live light oil–pure CO$_2$ system in the nanopores of 4 nm at $T_{res} = 53.0^\circ$C.
different pressures and $T_{\text{res}} = 53.0^\circ\text{C}$ are plotted in Figure 5.4b. It should be noted that an obvious IFT drop occurs starting from 1,000 nm at $P = 4.0 \text{ MPa}$ while starting from 100 nm at $P = 7.5$ and $9.5 \text{ MPa}$. Thus it is inferred that the IFT is more sensitive to the variation of the pore radius at a lower pressure. In other word, the confinement effect on the IFT tends to be weaker at a higher pressure.

In Figures 5.5a–c, the MMPs of the Pembina live light oil–pure CO$_2$ system in the nanopores with pore radius of 100, 20, and 4 nm are determined to be 15.4, 13.7, and 13.4 MPa by using the LCC criterion from the DIM at $T_{\text{res}} = 53.0^\circ\text{C}$, which are listed and compared with the measured MMPs from the slim-tube tests (Zhang and Gu, 2015) for bulk phase in Table 5.6. It is found that the MMPs of the Pembina live light oil–pure CO$_2$ system in bulk phase and in nanopore with pore radius of 100 nm are almost same. The MMPs are found to be decreased with a decrease of pore level when the pore radius is smaller than 100 nm. Furthermore, the MMPs of the Bakken live light oil–pure CO$_2$ system in the nanopores with the three same pore radius are determined to be 24.1, 21.4, and 20.6 MPa at $T_{\text{res}} = 116.1^\circ\text{C}$ and shown in Figures 5.6a–c. On the other hand, the MMP of the Bakken live light oil–pure CO$_2$ system in bulk phase is estimated to be 24.7 MPa by using the multiple-mixing cell method in CMG WinProp module and listed in Table 5.6. Thus it is concluded that the decrease of pore radius (i.e., increase of the confinement effect) lowers the MMPs significantly for the both Pembina and Bakken live light oil–pure CO$_2$ systems.

In comparison with the literature results, the determined MMPs of the Bakken live light oil–pure CO$_2$ system from the DIM in this study are higher either in bulk phase or in nanopores. It is inferred that the literature results were underestimated and the determined MMPs from the DIM are more accurate, which is concluded based on the following two
Table 5.6

Determined minimum miscibility pressures (MMPs) from the diminishing interface method (DIM) in the nanopores with different pore radius and measured/predicted bulk-phase MMPs from the slim-tube tests and multiple-mixing cell method for the Pembina live light oil–pure CO$_2$ system at 53.0°C and Bakken live light oil–CO$_2$ system at 116.1°C.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Gas</th>
<th>Temperature (°C)</th>
<th>Pore radius (nm)</th>
<th>MMP (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pembina live light oil</td>
<td>Pure CO$_2$</td>
<td>53.0</td>
<td>Inf (bulk phase)</td>
<td>15.2–15.4$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>15.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>13.4</td>
</tr>
<tr>
<td>Bakken live light oil</td>
<td>Pure CO$_2$</td>
<td>116.1</td>
<td>Inf (bulk phase)</td>
<td>24.7$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Notes:  
$^a$: determined from the slim-tube tests  
$^b$: calculated from the multiple-mixing cell method
Figure 5.6a Determined minimum miscibility pressures of the Bakken live light oil–pure CO$_2$ system in the nanopores of 100 nm at $T_{res} = 116.1^\circ$C.
Figure 5.6b Determined minimum miscibility pressures of the Bakken live light oil–pure CO₂ system in the nanopores of 20 nm at $T_{res} = 116.1\,^\circ C$. 

MMP = 21.4 MPa
Figure 5.6c Determined minimum miscibility pressures of the Bakken live light oil–pure CO₂ system in the nanopores of 4 nm at $T_{\text{res}} = 116.1^\circ \text{C}$. 
reasons: first, the determined MMPs of the Pembina dead/live light oil–pure/impure CO₂ systems from the DIM in bulk phase agree well with the measured MMPs from some laboratory tests, which means the DIM together with the modified PR-EOS is accurate to determine MMPs; second, the calculated MMP of the Bakken live light oil–pure CO₂ system in bulk phase is 24.7 MPa, which is comparable to the determined MMPs from the DIM but much higher than the literature data. In addition, it should be noted that the MMPs of the Bakken live light oil–pure CO₂ system are much higher than those of the Pembina live light oil–pure CO₂ system either in bulk phase or in nanopores. This is because the feed oil and solvent ratio of the former system is 0.50:0.50 by mole while that of the latter system is 0.01:0.99 by mole. It means the amount of CH₄ and heavy components from the oil in the former system is much higher than that of the latter system. Besides, the reservoir temperature of the Bakken live light oil–pure CO₂ system is 116.1°C, which is much higher than 53.0°C for the Pembina live light oil–pure CO₂ system. Last but not least, the determined MMPs from the DIM are found to be more accurate in comparison with the calculated ones from some existing theoretical methods, whose technical details are presented in the APPENDIX I.

5.3 Nanoscale-Extended Correlation

Empirical correlations are always developed from statistical analyses of several important but normal parameters of the oil–gas system, which are available and appropriate to predict the MMPs in a sufficiently fast and relatively accurate manner (Adekunle and Hoffman, 2016). In general, the empirical correlation usually takes into account the reservoir temperature, oil composition, and gas composition because they are three important factors affecting the MMPs in bulk phase (Emera and Sarma, 2005). In the
literature, the MMP of an oil–gas system is always increased with temperature. More specifically, most studies found that the MMPs are linearly increased with the temperatures within a certain temperature range, whereas three different trends (i.e., concave downward, concave upward, and linear) of the MMPs for different oils as a function of temperatures was reported (Elsharkawy et al., 1996). In addition, the initial overall fluid composition is found to have a foremost and direct effect on the MMP (Hemmati-Sarapardeh et al., 2013). In practice, the initial oil composition effect was studied by comparing the measured MMPs of different oil samples with the same solvent phase (e.g., CO₂) while the injection gas composition effect was studied by choosing different solvent phases with the same oil sample. For example, the CH₄-dominated hydrocarbons (HCs) pre-saturated live light oil–CO₂ system was found to have a higher MMP, whereas the intermediate HCs pre-saturated one has a lower IFT/MMP in comparison with that of the dead light oil–CO₂ system (Zhang et al., 2017b, 2017a). Similar results were also found for the effects of injection gas compositions on the MMP studies (Wang et al., 2015).

In petroleum industry, numerous empirical correlations have been developed to predict the MMPs. However, most of them are not applicable for a general use but always limited to some specific oil–gas systems. Furthermore, most correlations are insensitive to the injection gas compositions and cannot accurately predict the MMPs with the impure gas solvents. More importantly, no correlation so far has been found to be capable of predicting the MMPs in nanopores. Therefore, it is of fundamental and practical importance to develop an accurate and reliable correlation for calculating the MMP for different oil–gas systems in bulk phase and nanopores. In this study, a new nanoscale-extended correlation is developed by taking into account of the reservoir temperature, oil and gas compositions,
and pore radius to calculate the MMPs in bulk phase and nanopores. The new correlation is analyzed and applied to calculate a total of 101 oil–gas MMPs for fifteen oil samples and thirteen gas solvents in bulk phase and nanopores, which are compared with and verified by those from some experimental methods and commonly-used existing correlations.

5.3.1 Experimental section

In this study, the detailed compositional analysis results of the fifteen oil samples and thirteen gas samples are listed in Tables 5.7a and b (Eakin and Mitch, 1988; Li et al., 2012; Shang et al., 2014; Teklu et al., 2014a; Zuo et al., 1993), wherein three oil and gas samples are proposed here and other samples were documented in the literature (Teklu et al., 2014a; Zhang, 2016). It can be seen from Table 5.7a that the selected oil samples are various and representative regarding the tight oil, which cover the dead and live oil samples as well as a wide content range of volatile (i.e., 0.00–66.35 mol.%), intermediate (i.e., 2.67–40.76 mol.%), and C\textsubscript{7+} components (i.e., 5.62–97.33 mol.%). In addition, the thirteen gas samples used here also represent a series of typical injection gas samples to enhance tight oil recovery, they are lean gas (e.g., pure N\textsubscript{2} or CH\textsubscript{4}), mixed gas (e.g., CO\textsubscript{2}+CH\textsubscript{4} or CO\textsubscript{2}+C\textsubscript{2}–6), and enriched gas (e.g., pure H\textsubscript{2}S or C\textsubscript{2}–6) samples. The detailed experimental setups and procedures for preparing the live oil sample and the impure gas solvent sample were described in the literature (Zhang, 2016). It should be noted that all the MMPs of the aforementioned oil–gas systems in bulk phase were measured from various experimental methods and/or recorded in the literature. For example, the MMPs of the oil A–gas A, oil B–gas A, and oil A–gas B systems are measured by using the coreflood tests, slim-tube tests, and VIT technique at the reservoir conditions, respectively (Zhang, 2016).
Table 5.7a

Compositional analysis results of fifteen crude oil samples used, three from this study and twelve from the literature (Li et al., 2012; Shang et al., 2014; Zuo et al., 1993; Eakin and Mitch, 1988; Teklu et al., 2014b).

<table>
<thead>
<tr>
<th>Component</th>
<th>Oil A</th>
<th>Oil B</th>
<th>Oil C</th>
<th>Oil D</th>
<th>Oil E</th>
<th>Oil F</th>
<th>Oil G</th>
<th>Oil H</th>
<th>Oil I</th>
<th>Oil J</th>
<th>Oil K</th>
<th>Oil L</th>
<th>Oil M</th>
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<td>0.00</td>
<td>1.77</td>
<td>1.97</td>
<td>2.13</td>
<td>0.00</td>
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<td>0.01</td>
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<td>0.34</td>
<td>0.48</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.17</td>
<td>1.41</td>
<td>6.66</td>
<td>0.36</td>
<td>0.81</td>
<td>1.34</td>
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<tr>
<td>C₁</td>
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<td>27.12</td>
<td>16.74</td>
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<td>Li</td>
<td>Shang</td>
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<td>Shang</td>
<td>Zou</td>
<td>E&amp;M</td>
<td>E&amp;M</td>
<td>Teklu</td>
<td>Teklu</td>
<td>Teklu</td>
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</tbody>
</table>

Notes: a: Estimated by using Eq. (6.43)
Table 5.7b

Compositional analysis results of thirteen gas solvent samples in addition to the pure CO$_2$ sample used, three from this study and ten from the literature (Shang et al., 2014; Eakin and Mitch, 1988; Teklu et al., 2014b).

<table>
<thead>
<tr>
<th>Component</th>
<th>Gas A</th>
<th>Gas B</th>
<th>Gas C</th>
<th>Gas D</th>
<th>Gas E</th>
<th>Gas F</th>
<th>Gas G</th>
<th>Gas H</th>
<th>Gas I</th>
<th>Gas J</th>
<th>Gas K</th>
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<td>90.00</td>
<td>90.00</td>
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<td>References</td>
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<td>This study</td>
<td>This study</td>
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<td>E&amp;M</td>
<td>E&amp;M</td>
<td>E&amp;M</td>
<td>Teklu</td>
<td>Teklu</td>
<td>Teklu</td>
<td>Teklu</td>
</tr>
</tbody>
</table>
A total of five respective coreflood and slim-tube tests were conducted to measure the MMPs in the previous study (Zhang and Gu, 2015). The composite reservoir core plugs used in the five coreflood tests were 8–10” long and 2” in diameter. In each coreflood test, CO$_2$ was injected at a constant volume injection rate of 0.4 cc/min and it was terminated after a total of 2.0 PV was injected until no more oil was produced. The slim tube has an inner diameter of 0.457 cm, a length of 12.2 m, and a total pore volume of 81.7 cm$^3$, which is packed with the Ottawa silica sands of 75–106 mesh. The measured average permeability and porosity were equal to 5.8 D and 41.0%, respectively. Pure CO$_2$ was injected into the slim tube to recover the oil at a constant volume flow rate of 0.1 cc/min and each slim-tube test was terminated after 1.2 PV of pure CO$_2$ was injected. On the other hand, the VIT technique is applied to determine the MMPs on a basis of the measured IFTs. The IFTs between the oil and gas were measured by applying the axisymmetric drop shape analysis (ADSA) technique for the pendant drop case (Zhang and Gu, 2016b). The high-pressure IFT cell is rated to 69.0 MPa and 177.0$^\circ$C, whose volume is 49.5 cm$^3$. The ADSA program requires the density difference between the oil drop and the gas phase at the test conditions and the local gravitational acceleration as the input data. The dead/live oil sample densities at different test conditions were measured and the CO$_2$ density was predicted by using the CMG WinProp module (Version 2016.10, Computer Modelling Group Limited, Canada). The measured oil recovery factor from the coreflood and slim-tube tests and the measured IFTs are plotted versus the pressure to determine the MMPs. By means of some existing MMP criteria (Zhang, 2016), the MMPs of the oil A–gas A, oil B–gas A, and oil A–gas B systems are determined to be 12.4, 15.4 and 21.8 MPa from the coreflood tests, slim-tube tests, and VIT technique at $T = 53.0^\circ$C, respectively.
5.3.2 Existing empirical correlations

In the literature, almost all existing empirical correlations for predicting the MMPs are generally expressed in mathematical equations and graphical formats (Valluri et al., 2017), the former of which occupy the most and to be specifically studied here. Reservoir temperature, oil composition, and injection gas composition are considered as three important factors affecting the MMP. Therefore, the existing correlations are reviewed and categorized as a function of the three important factors: Type I—temperature dependent (Lee, 1979; Orr Jr and Jensen, 1984; Yellig and Metcalfe, 1980), Type II—temperature and oil composition dependent (Holm and Josendal, 1974; Huang et al., 2003; Mungan, 1981), and Type III—temperature, oil composition, and gas composition dependent (Ahmadi et al., 2017; Shokir, 2007; ZareNezhad, 2016). A detailed summary of 40 commonly-used existing correlations for predicting the MMPs are analyzed and listed in the APPENDIX II.

The reservoir temperature has always been considered as the most important factor affecting the MMP and all the existing correlations own the term of temperature. In early years, some correlations were developed as only a function of the temperature. The MMP was considered to be linearly increased with the temperature (i.e., 10–20 psi/°F incremental) at the beginning, whereas at a later time, the MMP was found to reach the maximum at a relatively higher temperature and the trend reverses afterwards. This concave downwards trend between the MMP and temperature has been verified by the experimental findings (Elsharkawy et al., 1996) and theoretical work (Yuan et al., 2004). In addition, various parameters are employed to reflect the effects of the oil and injection gas compositions on the MMP. More specifically, the molecular weights of $C_{5+}$ ($MW_{C5+}$) or $C_{7+}$ ($MW_{C7+}$) of the oil sample as well as the mole fractions of the volatile and/or intermediate components
of the oil and gas samples are taken into account for some existing MMP correlations. Five typical correlations are selected and introduced in details to better understand the applications of the empirical correlations for predicting the MMPs, first of which is the original Alston’s correlation and takes the following form (Alston et al., 1985),

\[
MMP = 6.0536 \times 10^{-6} (1.8T_R + 32)^{1.06} (MW_{C5+})^{1.78} \left( \frac{x_{\text{VOL}}}{x_{\text{INT}}} \right)^{0.136}
\] (5.32)

where \(T_R\) is the reservoir temperature; \(x_{\text{VOL}}\) is the mole fraction of volatile components including \(N_2\) and \(CH_4\); and \(x_{\text{INT}}\) is the mole fraction of intermediate components including \(CO_2\), \(H_2S\), and \(C_2-C_4\). The Alston’s correlation was verified for limited data with the \(MW_{C5+}\) up to 302.5 g/mol, temperatures less than 90 °F (326.7 K), and pressure range of 1000–2500 psia (6.9–17.2 MPa) in the original literature (Alston et al., 1985). Later, Li et al. (2012) modified the original Alston correlation for predicting MMPs of different dead and live oil–\(CO_2\) systems as follows,

\[
MMP = 7.30991 \times 10^{-5} \left[\ln(1.8T_R + 32)\right]^{5.33647} \left[\ln(MW_{C7+})\right]^{2.08836} \left(1 + \frac{x_{\text{VOL}}}{x_{\text{INT}}}\right)^{2.01658 \times 10^{-1}}
\] (5.33)

It is worthwhile to mention that the Li’s correlation was verified for limited data with the \(MW_{C7+}\) up to 402.7 g/mol and temperatures less than 115.56 °C (388.71 K) in the original literature (Li et al., 2012). In addition, Yuan et al. (2005) used an analytical theory from the EOS to generate the following correlation to calculate the MMPs for the pure and impure \(CO_2\),

\[
MMP_{\text{pure}} = a_1 + a_2MW_{C7+} + a_3x_{C_2+} + (a_4 + a_5MW_{C7+} + a_6\frac{x_{C_2+}}{MW_{C7+}})T_R
\]

\[
+ (a_7 + a_8MW_{C7+} + a_9MW_{C7+} + a_{10}x_{C_2+})T_R^2
\] (5.34)
\[
\frac{\text{MMP}_{\text{imp}}}{\text{MMP}_{\text{pure}}} = 1 + m(y_{\text{CO}_2} - 100) \quad (5.35)
\]

\[m = a_1 + a_2M\text{W}_{\text{C}_7} + a_3x_{\text{C}_{2-6}} + (a_4 + a_5M\text{W}_{\text{C}_7} + a_6\frac{x_{\text{C}_{2-6}}}{M\text{W}_{\text{C}_7}})T_R + (a_7 + a_8M\text{W}_{\text{C}_7} + a_9M\text{W}_{\text{C}_7} + a_{10}x_{\text{C}_{2-6}})T_R^2\]

where \(\text{MMP}_{\text{pure}}\) is the predicted MMP for pure \(\text{CO}_2\) injection; \(\text{MMP}_{\text{imp}}\) is the predicted MMP for impure \(\text{CO}_2\) injection; \(x_{\text{C}_{2-6}}\) is the mole fraction of \(\text{C}_2-\text{C}_6\) in oil; \(a_i\) is the empirical coefficient, \(i = 1...10\); and \(y_{\text{CO}_2}\) is the mole fraction of \(\text{CO}_2\) in injection gas.

Recently, two correlations were developed/modified to predict the pure and impure \(\text{CO}_2\) MMPs, first of which is the Shang’s correlation (Shang et al., 2014),

\[
\text{MMP} = \exp\{((T_R^b + g)[\ln(M\text{W}_{\text{C}_7})]f_i + h(\exp(\frac{X_{\text{VOL}}}{X_{\text{INT}}}))^d_i + i)(x_{\text{C}_{7+}})^f\} \quad (5.36)
\]

\[
\text{MMP} = \exp\{aT_R^bE^fX_{\text{CO}_2} + D^mX_{\text{H}_2}\text{S}^jX_{\text{CH}_4}d^gX_{\text{C}_7}^c - g^y_{\text{H}_2\text{S}} - h^y_{\text{C}_2-\text{C}_7}\} \quad (5.37)
\]

\[
\text{MMP} = (aT_R^b + E^fD^j(\exp(x_{\text{CO}_2}))^g)(x_{\text{C}_{7+}})^d(h^y_{\text{H}_2\text{S}} i^y_{\text{C}_2-\text{C}_7} + j) + T_R^m
\]

\[E = (M\text{W}_{\text{C}_7})^{\frac{2}{VOL/\text{INT}}}
\]

\[D = \exp(x_{\text{N}_2})\exp(x_{\text{CH}_4})/\exp(x_{\text{CO}_2})\]

Eqs. (5.36), (5.37), and (5.38) are used to calculate the MMPs for pure \(\text{CO}_2\), \(y_{\text{CO}_2} < 0.5\), and \(y_{\text{CO}_2} > 0.5\), respectively, where \(x_{\text{C}_{7+}}\) is the mole fraction of \(\text{C}_{7+}\) in oil; \(x_{\text{N}_2}\), \(x_{\text{CH}_4}\), \(x_{\text{H}_2\text{S}}\), \(x_{\text{C}_{2-\text{C}_7}}\) is \(\text{N}_2\), \(\text{CH}_4\), \(\text{H}_2\text{S}\), and \(\text{C}_2-\text{C}_7\) mole fraction in injection gas; and \(a\), \(b\), \(c\), \(d\), \(f\), \(g\), \(h\), \(i\), \(j\), and \(m\) are empirical coefficients. In addition, Valluri et al. (2017) developed an optimized power law model as shown,

\[
\text{MMP} = 0.3123T_R^{0.9851}M\text{W}_{\text{C}_{7+}}^{0.7421} \quad (5.39)
\]
Table 5.8

Comparison of calculated minimum miscibility pressures (MMPs) from five existing correlations and determined MMPs from the literature in bulk phase and the nanopores with different pore radius for the Pembina dead and live light oil–pure and impure CO₂ systems at 53.0°C and Bakken live light oil–CO₂ system at 116.1°C.

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<th>Valluri et al.</th>
<th>Li et al.</th>
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<td>57.14</td>
<td>21.7</td>
<td>34.78</td>
<td>24.2</td>
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</tr>
<tr>
<td></td>
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<td>20</td>
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<td>21.7</td>
<td>36.48</td>
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</tr>
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<td>4</td>
<td>14.1</td>
<td>25.3</td>
<td>79.43</td>
<td>21.7</td>
<td>53.90</td>
<td>24.2</td>
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<table>
<thead>
<tr>
<th>AAD (%)</th>
<th>MAD (%)</th>
</tr>
</thead>
<tbody>
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<td></td>
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</tr>
</tbody>
</table>

Notes:
MMP_{det} Determined MMPs from literature
The above-mentioned five correlations are applied to calculate the MMPs of the Pembina dead and live light oil–pure and impure CO\textsubscript{2} systems and Bakken live light oil–CO\textsubscript{2} system in bulk phase and nanopores at the reservoir conditions, whose results are summarized, listed, and compared with the measured/predicted MMPs in Table 5.8. It is found that the five existing correlations seems to be insensitive to the oil/gas compositional change to different extents in bulk phase because the percentage absolute deviations (AD\%) between the calculated and measured MMPs become larger for the live oil or impure CO\textsubscript{2} case. More importantly, the five existing correlations cannot calculate the MMPs in nanopores since the calculated MMPs remain unchanged regardless of different pore radii. Hence, it is necessary to develop an empirical correlation for calculating the MMPs of different oil–gas systems in nanopores.

5.3.4 Mathematical formulation

Factors affecting the MMP

The reservoir temperature, oil and gas compositions are the three important factors for the MMP correlations as aforementioned, whose effects on the MMPs are specifically studied by means of the determined MMPs of the Pembina and Bakken live and dead oil–pure and impure CO\textsubscript{2} systems from the diminishing interface method (DIM) (Zhang et al., 2017a; Zhang et al., 2017b) at the different pore radii and temperatures. The detailed results are listed in Table 5.9 and plotted in Figures 5.7–5.9. In the previous study, the MMP was correlated with the reservoir temperature to be a concave downwards parabola curve within a wide temperature range from 140 to 750°F (i.e., 60 to 399°C): 

\[
MMP(\text{psi}) = -0.0211T^2(F) + 17.446T + 549.25 \quad (R^2 = 0.9810).
\]

It means the MMP is increased with the temperature at low temperatures, reaches a maximum, and then
Table 5.9
Summary of the determined minimum miscibility pressures from the diminishing interface method for the Pembina dead and live light oil–pure and impure CO₂ systems and Bakken live light oil–pure and impure CO₂ systems at the pore radius of 10 nm and different temperatures.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Gas (mol.%)</th>
<th>T (°C)</th>
<th>MMP (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100.00 CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>15.6</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.0</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>53.0</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80.0</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>116.1</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150.0</td>
<td>29.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200.0</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>250.0</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
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<td>300.0</td>
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</tr>
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<td>45.2</td>
</tr>
<tr>
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<td>100.00 CO₂</td>
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<td>14.8</td>
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<tr>
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<td>10.00 CO₂ + 90.00 CH₄</td>
<td>53.0</td>
<td>38.7</td>
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Figure 5.7 Temperature effect on the recorded MMPs in bulk phase from the literature (Yuan et al., 2005) and the determined MMPs at the pore radius of 10 nm for the Pembina dead and live oil–pure CO₂ systems in this study.
Figure 5.8 Correlation between molecular weights of C₅⁺ and C₇⁺ for fifteen different oil samples used in this study.
Figure 5.9a Determined minimum miscibility pressures of the Pembina dead and live oil–
pure CO₂ systems at $T = 53.0^\circ$C and $116.1^\circ$C and the pore radius of 10 nm.
Figure 5.9b Determined minimum miscibility pressures of the Pembina live oil and Bakken live oil—pure and impure CO₂ systems with six different CH₄ contents \((y_{\text{CH}_4} = 0, 0.10, 0.35, 0.50, 0.65, 0.90)\) at \(T = 53.0^\circ\text{C}\).
decreases with the temperature at high temperatures (Yuan et al., 2005). Two similar trends between the MMPs of the Pembina dead and live oil–pure CO\textsubscript{2} systems and temperatures are obtained and plotted in Figure 5.7. It is found that the MMPs of these two oil–gas systems are almost linearly increased with the temperature to approximate 200°C and decrease with the temperature afterwards. On a basis of the data points in this figure, the MMPs for the two oil–CO\textsubscript{2} systems at different temperatures are correlated to the temperature \( T \) (C) by using the quadratic regression:

Pembina dead oil case \[ \text{MMP/MPa} = -0.0007 \left( T / C \right)^2 + 0.2850 T + 1.0055 \] \textbf{(6.40)}

Pembina live oil case \[ \text{MMP/MPa} = -0.0008 \left( T / C \right)^2 + 0.3355 T + 0.5074 \] \textbf{(6.41)}

The above-mentioned result, which is the MMP linearly increases with the temperature at low temperatures while decreases with the temperature at high temperatures, is attributed to the phase change at extremely high temperatures (Seo et al., 2014). Hence, it is physically meaningful that the MMP will not increase to the infinite even if the temperature is continuously increased.

As an important parameter of the oil sample, \( MW_{C5+} \) or \( MW_{C7+} \) is a necessary part of the MMP correlation in order to consider the oil composition effect (Kumar and Okuno, 2013). In the literature, \( MW_{C5} \) can be obtained by means of the graphical correlation (Lasater, 1958) or directly calculated from an empirical correlation in terms of the API gravity of the oil sample as follows (Holtz et al., 2006),

\[ MW_{C5+} = \left( \frac{7864.9}{API} \right)^{0.9628} \] \textbf{(5.42)}

Figure 5.8 shows the \( MW_{C5+} \) and \( MW_{C7+} \) of different oil samples from the literature, which are found to be highly correlated (i.e., \( R^2 = 0.9832 \)) by a linear trend in the following
The oil composition effects on the determined MMPs are summarized in Figure 5.9a. First, it is found that the oil composition effects on the determined MMPs are measurable but marginal at a constant temperature. Second, the MMP increases from 11.6 to 13.7 MPa at \( T = 53.0^\circ\text{C} \) and from 26.5 to 29.7 MPa at \( T = 116.1^\circ\text{C} \) when the oil sample is changed from dead to live oil with the addition of the CH\(_4\)-dominated produced gas (Zhang et al., 2017a). A larger MMP increase occurs at a higher temperature and the pore radius of 10 nm. Hence, the MMP is found to be more sensitive to the initial oil composition at a higher temperature. In an oilfield CO\(_2\) injection project, the injected pure CO\(_2\) will likely contain some solution gas, the primary component of which is CH\(_4\) (Alfarge et al., 2017). In Figure 5.9b, the MMPs of the Pembina live oil–impure CO\(_2\) system are determined to be 17.2, 26.3, 31.0, 36.2, and 45.2 MPa from the DIM and the MMPs of the Bakken live oil–impure CO\(_2\) system are determined to be 17.5, 24.1, 28.1, 31.8, and 38.7 MPa at \( T = 53.0^\circ\text{C} \) when the CH\(_4\) content increases from 0.10, 0.35, 0.50, 0.65, to 0.90 in mole fraction. It is obvious that the additions of CH\(_4\) can significantly increase the MMP. On a basis of the data points in this figure, the MMPs are linearly correlated to the amounts of the CH\(_4\) addition in an impure CO\(_2\) sample in mole fraction:

Pembina live oil case \[ \frac{MMP}{MPa} = 34.8590\, y_{\text{CH}_4} + 13.7329 \] (5.44)

Bakken live oil case \[ \frac{MMP}{MPa} = 26.4285\, y_{\text{CH}_4} + 14.8133 \] (5.45)

The above two correlations show that the MMP is rather sensitive to the CH\(_4\) content in gas phase and it is increased linearly with CH\(_4\) content up to 0.90 mole fraction. More specifically, the MMP increases linearly with an increasing CH\(_4\) content at the approximate
rates of 0.3486 MPa and 0.2643 MPa per 0.01 CH$_4$ additions for the Pembina and Bakken live oil, respectively. On the other hand, some additions of the intermediate HCs (e.g., C$_2$–C$_6$) into the oil or gas phase may be beneficial for the miscibility development and cause the MMP reductions (Chowdhary and Ladanyi, 2008).

In addition to the above-mentioned three important factors, effect of the pore radius on the MMP cannot be ignored, especially in the tight oil formations (Zhang et al., 2017b). In this study, the MMPs of the Pembina and Bakken live oil–pure CO$_2$ systems at different pore radius ranging from the infinite (i.e., 1,000,000 nm) to 4nm and $T_R = 53.0$ and 116.1°C are determined from the DIM (Zhang et al., 2017b) and listed in Table 5.8, which are also plotted versus the pressure in Figure 5.10. It is easily seen that the MMP remains constant until the pore radius is reduced to 100 nm and decreases with the further reduction of the pore radius afterwards. This pattern is in good agreement with and verified by the measured/predicted results from the experiment/theoretical work in the literature (Teklu et al., 2014b; Wang et al., 2014), which is mainly attributed to the strengthened capillary pressure and shifts of the critical properties in the nanopores. Overall, the reservoir temperature, oil and gas compositions, and pore radius are concluded to be the most important four factors affecting the MMPs of the oil–gas systems in nanopores.

5.3.5 New MMP correlation

In the previous section, the five typically existing correlations are briefly introduced and applied to calculate the MMPs. It is obvious that the Yuan’s correlation works the best due to its lowest percentage average absolute deviation (AAD%) and second lowest maximum absolute deviation (MAD%). However, ten respective numerical coefficients are required in the Yuan’s correlation for predicting the pure CO$_2$ and impure CO$_2$ MMPs,
Figure 5.10 Determined minimum miscibility pressures of the Pembina and Bakken live oil–pure CO$_2$ systems at different pore radius and $T_{res} = 53.0$ and 116.1°C.
which may give better results mainly due to its complex mathematical formulation. The same problem is also noticed for the Shang’s correlation. Although an overall good results can be obtained by using the Valluri’s correlation in Table 5.8, it gives the same results for the first three different oil–gas systems. It is inferred that the Valluri’s correlation can be used to calculate the MMPs for several limited oil–gas systems because it only has two parameters. On the other hand, the Li’s correlation, as a modified Alston’s correlation, is shown in Eq. (5.33) and found to be physically meaningful and fairly accurate for the MMP calculation. Thus, the new correlation in this study is developed on a basis of the Li’s correlation and shown as follows,

\[
MMP = a[\ln(1.8T_R + 32)]^{y} [\ln(MW_{CS})]^{x} (1 + \frac{x_{VOL} + y_{VOL}}{x_{INT} + y_{INT}})^{d} + e \ln(r_p)^2 + f \ln(r_p^{'})(5.46)
\]

where \(y_{VOL}\) is the mole fraction of volatile components including \(N_2\) and \(CH_4\) in injection gas; and \(y_{INT}\) is the mole fraction of intermediate components including \(CO_2\), \(H_2S\), and \(C_2–C_4\) in injection gas; \(r_p\) is the pore radius; and \(a, b, c, d, e, \) and \(f\) are empirical coefficients.

In the new correlation, the effect of reservoir temperature on the MMP is still expressed as the term \(\ln(1.8T_R + 32)\). This is because the geothermal gradient is about 25°C/km in the continental and oceanic lithosphere (Fridleifsson et al., 2008), whose depth are in the respective ranges of 40–280 and 50–140 km (Barrell, 1914). It means the reservoir temperatures of the both conventional and unconventional oil reservoirs follow the geothermal gradient of 25°C/km. Figure 5.7 shows that the MMP is almost linearly increased with the reservoir temperature until 200°C. In other word, the MMP and reservoir temperature always have a linear correlation when the depth of the reservoir is shallower.
than 8,000 m, where most tight oil reservoirs exist within the range. The natural logarithm is used to control the temperature effect when the reservoir temperature becomes relatively high, which can also be verified by Figure 5.7 that the rate of the MMP increase at relatively high temperatures ($T < 200 \, ^\circ C$) tends to be lower. In the new correlation, $MW_{C5^+}$ instead of $MW_{C7^+}$ is used because it can be directly calculated from the empirical correlation in Eq. (5.42). It is also found from Figure 5.8 and Eq. (5.43) that the $MW_{C5^+}$ and $MW_{C7^+}$ have a highly linear correlation. Thus, it makes no difference to choose either $MW_{C5^+}$ or $MW_{C7^+}$ because a numerical coefficient is employed with the term $\ln(MW_{C5^+})$.

In comparison with the original Alston’s correlation, the term $(1 + \frac{x_{VOL}}{x_{INT}})$, instead of $(\frac{x_{VOL}}{x_{INT}})$, is regarded as a correction term to differentiate the MMPs for the live and dead oil samples because normally, the dead oils don’t have volatile components (Gonzalez et al., 2012). This modification essentially corrects the calculated MMPs for dead and live oils. On the other hand, the injection gas composition also affects the MMP as aforementioned. However, as illustrated in Table 5.8, the same MMP for the pure and impure CO$_2$ cases are calculated from the Li’s correlation. Moreover, Figure 5.11 also shows that the term $(1 + \frac{x_{VOL}}{x_{INT}})$ cannot quantify the properties of the injection gas samples by generating the same result for different injection gas samples. Obviously, a constant MMP for the pure and impure CO$_2$ cases is physically incorrect, which is also validated by the measured MMPs in Tables 5.8 and 5.9 as well as abundant literature results (Li et al., 2012; Shang et al., 2014; Zuo et al., 1993; Eakin and Mitch, 1988). Hence, in the new correlation, the term
Figure 5.11 Comparison of the calculated minimum miscibility pressures of various oil–
pure and impure gas solvent systems from the Li’s correlation (Li et al., 2012) with the
term $(1 + \frac{x_{\text{vol}}}{x_{\text{int}}})$ and the newly-developed correlation with the term $(1 + \frac{x_{\text{vol}} + y_{\text{vol}}}{x_{\text{int}} + y_{\text{int}}})$.  

$1 + \frac{x_{\text{vol}}}{x_{\text{int}}} \text{ or } 1 + \frac{x_{\text{vol}} + y_{\text{vol}}}{(x_{\text{int}} + y_{\text{int}})}$ vs. MMP
\[(1 + \frac{x_{\text{VOL}} + y_{\text{VOL}}}{x_{\text{INT}} + y_{\text{INT}}}) \text{ is used to represent the effects of the oil and injection gas compositions on the MMP, whose results are compared with those of the term } (1 + \frac{x_{\text{VOL}}}{x_{\text{INT}}}) \text{ in Figure 5.11.} \]

It is found that the MMP is almost linearly increased with the amount of the volatile components in the oil and/or gas phases, which is physical correct and agrees well with Figures 5.9a and b and the literature results (Zhang et al., 2017b, 2017a). In addition, the term \(e \ln(r_p)^2 + f \ln(r_p)\) is added to consider the effect of the pore radius in the new correlation. The natural logarithm is used because the MMP has a significant change only at an extremely small pore radius, especially when \(r_p\) is smaller than 100 nm. The empirical coefficients in Eq. (5.46) are obtained by using the non-linear least-square method (MathWorks, 2016) and the new nanoscale-extended MMP correlation is finalized as follows,

\[
MMP = 2.5562 \times 10^{-3} \left[\ln(1.8 T_R + 32)\right]^{1.1945} \left[\ln(MW_{C5+})\right]^{1.0724} (1 + \frac{x_{\text{VOL}} + y_{\text{VOL}}}{x_{\text{INT}} + y_{\text{INT}}})^{0.6579} \\
+ 2.9945 \times 10^{-4} \ln(r_p)^2 + 2.0620 \times 10^{-1} \ln(r_p) \tag{5.47}
\]

Eq. (5.47) is the new nanoscale-extended MMP correlation, which is applied to calculate the MMPs of various dead and live oil–pure and impure CO\(_2\) systems in bulk phase and nanopores in the following section.

### 5.3.6 Results and discussion

The newly-developed nanoscale-extended correlation, i.e., Eq. (5.47), is applied to calculate the MMPs and compared with some experimental methods (e.g., coreflood and slim-tube tests and VIT technique) as well as the several commonly used correlations documented in the literature. Table 5.10a shows the comparison of pure CO\(_2\) MMPs from
<table>
<thead>
<tr>
<th>Oil</th>
<th>$T$ (°C)</th>
<th>MMP_{pea} (MPa)</th>
<th>This study</th>
<th>Shang et al.,</th>
<th>Valluri et al.,</th>
<th>Li et al.,</th>
<th>Yuan et al.,</th>
<th>Alston et al.,</th>
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<td></td>
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<td>MPa AD%</td>
<td>MPa AD%</td>
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<td>MPa AD%</td>
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Table 5.10b
Comparison of calculated pure and impure gas minimum miscibility pressures (MMPs) from the newly-developed and four existing correlations as well as the measured MMPs from the literature in bulk phase for 27 different oil–gas systems at different temperatures.

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AAD (%) – 4.70 – 30.68 – 68.50 – 107.76 – 43.40
MAD (%) – 15.81 – 155.32 – 358.43 – 937.84 – 170.37
the new correlation and experimental methods as well as seven existing correlations for fifteen different oil samples in bulk phase at different temperatures. It is easily seen that in comparison with the existing correlations, the newly-developed correlation provides the most accurate MMPs with an overall AAD% of 5.72% and MAD% of 12.96%, both of which are the lowest and outperform the existing correlations in Table 5.10a. More specifically, the respective AAD% for the dead and live oil samples from the new correlation are 6.36% and 5.47%, which means the new correlation has a consistently good performance for the either dead or live oil sample. It should be noted that among the seven existing correlations, the Li’s correlation provides a comparable accuracy with an AAD% of 11.43% and a MAD% of 49.43%.

In Table 5.10b, the newly-developed correlation is applied to calculate the MMPs of various oil–pure and impure gas solvent systems in bulk phase at different temperatures, which are compared with the measured MMPs from the experimental methods and the calculated MMPs from the four popular existing correlations. It is found that the new correlation, in comparison with the existing correlations, is superior for calculating the different pure/impure gas solvent MMPs with an overall AAD% of 4.70% and MAD% of 15.81%. Some possible experimental error may exist and an accurate correlation should provide a calculate error within or close to the experimental error. Figure 5.12 shows the comparisons of the calculated MMPs from the new correlation versus the measured MMPs for various dead and live oil–pure and impure gas solvent systems in bulk phase. It is found that the calculated and measured MMPs are quite similar with the correlation coefficients of $R^2 = 0.9869$ for the pure CO$_2$ case and $R^2 = 0.9891$ for the impure gas case. Therefore, the newly-developed correlation is proven to be accurate for calculating the MMPs of
Figure 5.12 Comparison of the calculated minimum miscibility pressures (MMPs) from the newly-developed correlation in this study and measured MMPs from the literature for various dead and live oil–pure and impure gas solvent systems in bulk phase.
Figure 5.13 Comparison of the calculated minimum miscibility pressures (MMPs) from the newly-developed correlation in this study and measured MMPs from the literature for various dead and live oil–pure and impure gas solvent systems in nanopores.
Table 5.11
Comparison of calculated minimum miscibility pressures (MMPs) from the newly-developed and measured MMPs from the literature in nanopores for 13 different oil–gas systems at different temperatures.

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different dead and live oil–pure and impure gas solvent systems in bulk phase.

Table 5.11 and Figure 5.13 compare the calculated MMPs from the new correlation and the recorded MMPs (Zhang et al., 2017a) in the literature for various dead and live oil–pure and impure gas solvent systems at pore radius of 100, 20, 10, and 4 nm and different temperatures. No calculated MMPs from the existing correlations are listed here because no existing correlations can calculate the MMPs in nanopores. It can be seen from Table 5.11 that the new correlation is able to accurately calculate the MMPs in nanopores with an overall AAD% of 6.91% and MAD% of 13.66%. It is worthwhile to mention that the calculated MMPs from the new correlation decreases with the reduction of pore radius, which follows the commonly-accepted observation/conclusion from the literature (Dong et al., 2016; Teklu et al., 2014b; Zhang et al., 2017a). However, the recorded MMPs of several oil–gas systems from the literature, for example, oil M, N, O–gas J and M systems, don’t follow this trend but change randomly with the pore radius. That is why the AD% between the calculated and recorded MMPs become slightly large. In summary, the newly-developed nanoscale-extended correlation is accurate, efficient, and physical correct to calculate the MMPs of various dead and live oil–pure and impure gas solvent systems in bulk phase and nanopores at different temperatures.

5.4 Summary

In Part I, first, the modified Peng–Robinson equation of state (PR-EOS) is found to be accurate for vapour–liquid equilibrium (VLE) calculations of the Pembina light oil–CO$_2$ system in bulk phase and the $iC_4$–$nC_4$–$C_8$ system and Bakken live light oil–pure CO$_2$ system in nanopores: in bulk phase, CO$_2$ dissolution is found to be a dominant mass-transfer process, which accounts for over 90% of the total compositional change. Moreover,
three pressure ranges, which are divided by $P^A$ and $P^B$, are identified and explained in
the two-phase compositions vs. pressure curves; in nanopores, the lighter components are
found to prefer to be in the vapour phase by increasing the temperature or decreasing the
pressure. Furthermore, the predicted capillary pressure in the nano-channel (100 nm) is
almost two orders of magnitude higher than that in the micro-channel (10 µm). Second, the
parachor model coupled with the modified PR-EOS is proven to be accurate for predicting
the interfacial tensions (IFTs) in bulk phase and nanopores: in bulk phase, the predicted
IFTs of the three Pembina light oil–CO$_2$ systems are found to agree well with the measured
IFTs at $T_{res} = 53.0^\circ$C. The predicted IFT is slightly lower at a relatively higher pressure,
which is because the light oil is not completely and accurately characterized in the EOS
modeling. For example, no heavy aromatic or asphaltic components are considered; in
nanopores, the predicted IFTs of the Bakken live light oil–pure CO$_2$ system agree well with
the recorded IFTs from the literature in the pore radius range of 4–1,000 nm at $T_{res} =
116.1^\circ$C. It is found that the IFT remains constant but decreases with the pore radius from
100 nm for Bakken oil case and from 1,000 nm for Pembina oil case. Moreover, the IFT is
more sensitive to the variation of the pore radius at a lower pressure for both two systems.
Third, a formula for the interfacial thickness between two mutually soluble phases (e.g.,
oil and CO$_2$), i.e., $\delta = (\frac{\partial \gamma}{\partial P})_T$, is developed by considering the two-way mass transfer, i.e.,
CO$_2$ dissolution into the oil through the convective dispersion and molecular diffusion and
hydrocarbons (HCs)-extraction from the oil phase by CO$_2$. Fourth, a new interfacial
thickness-based method, the diminishing interface method (DIM), is developed and applied
to determine the minimum miscibility pressures (MMPs) of different light oil–CO$_2$ systems
in bulk phase and nanopores by extrapolating the derivative of the interfacial thickness with respect to the pressure \( (\Delta S/\Delta P)_t \) to zero: in bulk phase, the MMPs of the Pembina dead light oil–pure CO\(_2\) system, live light oil–pure CO\(_2\) system, and dead light oil–impure CO\(_2\) system at \( T_{\text{res}} = 53.0^\circ\text{C} \) are determined to be 12.4, 15.0, and 22.1 MPa by using the linear correlation coefficient (LCC) criterion from the DIM, which agree well with 12.4–12.9 MPa from the coreflood tests, 15.2–15.4 MPa from the slim-tube tests, and 23.4–23.5 MPa from the rising-bubble apparatus (RBA) tests, respectively. The determined MMP from the DIM is found to be in good agreement with \( P^B \). Thus the determined MMP from the DIM is proven to be physically meaningful, at which not only the interfacial thickness between the light oil and CO\(_2\) phases tends to be minimum and stabilized with the pressure but the two-phase compositional change also reaches its maximum; in nanopores, the MMPs of the Pembina live light oil–pure CO\(_2\) system in the nanopores with pore radius of 100, 20, and 4 nm are determined to be 15.4, 13.7, and 13.4 MPa by using the LCC criterion from the DIM at \( T_{\text{res}} = 53.0^\circ\text{C} \). In addition, the MMP of the Bakken live light oil–pure CO\(_2\) system in bulk phase at \( T_{\text{res}} = 116.1^\circ\text{C} \) is estimated to be 24.7 MPa from multiple-mixing cell method and the MMPs in the nanopores with pore radius of 100, 20, and 4 nm are determined to be 24.1, 21.4, and 20.6 MPa, respectively. In comparison with the measured MMPs in bulk phase, the MMPs are found to be decreased with a decrease of pore level when the pore radius is smaller than 100 nm.

In Part II, a new nanoscale-extended correlation is developed to calculate the minimum miscibility pressures (MMPs) of different dead and live oil–pure and impure gas solvent systems in bulk phase and nanopores. A total of 40 existing correlations have been reviewed and categorized as a function of the following three important factors: Type I–temperature...
dependent, Type II–temperature and oil composition dependent, and Type III–temperature, oil composition, and gas composition dependent. No one existing correlation so far has been found to be applicable for calculating the MMPs in the nanopores. In bulk phase, the reservoir temperature, oil and gas compositions are three important factors on the MMPs. The MMPs are found to be correlated with the reservoir temperatures in a concave downwards parabola curve and linearly with the oil molecular weights of \( C_{5+} \) and \( C_{7+} \). Moreover, the MMPs are increased with the additions of lean gas (e.g., CH\(_4\) or N\(_2\)) but reduced by adding the intermediate HCs (e.g., C\(_2\)–C\(_6\)) into the oil or gas phase. In nanopores, the pore radius is a necessary factor to be considered for the MMP calculation in addition to the above-mentioned three factors. The MMP remains constant until the pore radius is reduced to 100 nm and decreases with the further reduction of the pore radius. The newly-developed correlation is accurate for calculating 61 oil–gas MMPs in bulk phase for the fifteen oil samples and thirteen gas solvents. In comparison with the seven existing correlations, the new correlation provides the most accurate MMPs with an overall percentage average absolute deviation (AAD%) of 5.72% and maximum absolute deviation (MAD%) of 12.96% for different dead and live oil–pure CO\(_2\) systems. Furthermore, for different oil–pure and impure gas solvent systems, the new correlation leads to the best calculation accuracy of the MMPs with an overall AAD% of 4.70% and MAD% of 15.81%. The newly-developed correlation is capable of calculating 40 oil–gas MMPs of different dead and live oil–pure and impure gas solvent systems in nanopores accurately, efficiently, and physical correctly. The overall AAD% and MAD% for the MMP calculations in nanopores from the new correlation are determined to be 6.91% and 13.66%, respectively.


CHAPTER 6 THERMODYNAMIC MISCIBILITY

DEVELOPMENTS

6.1 Introduction

Thermodynamic miscibility is a critical state that attracts great attentions in many practical applications, such as pharmaceutical dosage forms (Abbar and Nandibewoor, 2011), macromolecule materials (Yin et al., 2008), oil and gas productions (Al Hinai et al., 2018). In practice, the miscibility state is defined as a stable homogeneous mixture that exhibits macroscopic physicochemical properties of a single-phase fluid (Kariman Moghaddam and Saeedi Dehaghani, 2017). In theory, the miscible fluid is considered to be homogeneous on a scale equivalent to the range of intermolecular forces (Utracki, 2004). Obviously, homogeneity is a domain feature of the miscibility in terms of either macroscopic compositional or microscopic intermolecular properties, which is substantially contributed through the fluid interphase mass transfer (Nicholls et al., 1991). Achieving the miscibility is of great importance in various technical aspects. For example, in the petroleum industry, the miscibility development between the residual oil and injected gas is desired for a gas injection project in the oilfield worldwide (L. Jin et al., 2017). The minimum miscibility pressure (MMP), which is defined as the lowest operating pressure for the liquid and gas phases become miscible in any portions, is pre-requisite to ensure a successful miscible gas flooding process (Zhang et al., 2017b). Although the MMP is an accurate quantitative indicator for the fluid miscibility, it is usually restricted to distinguish the immiscible and miscible states.

In the chemical engineering, free energy of mixing and solubility parameter are two
available quantities for quantifying the fluid miscibility (Scatchard, 1931; Xavier et al., 2016). To form a miscible blend, the free energy of mixing should be negative and its second derivative with respect to the composition has to be positive (Bates, 1991). A more negative difference of the fluid free energy usually represents a better miscible state (Xavier et al., 2016). The solubility parameter, which describes a solvent affinity to a solute, was firstly introduced in 1950 (Hildebrand, 1936). The solubility parameter was a numerical value and derived from the cohesive energy density of the solvent initially, which was further modified and divided into three parts: a dispersion force component, a hydrogen bond component, and a polar component (Hansen, 1969). It should be noted that for the substances without polar and hydrogen-bonding effect, such as alkanes, the values of the one and three-component solubility parameters are equivalent (Barton, 1991). In the literature, some theoretical and/or numerical methods, such as the empirical correlation (Fedors, 1974) and equation of state (EOS) (Eslamimanesh and Esmaeilzadeh, 2010), have been proposed to calculate the free energy of mixing and solubility parameter. However, most previous calculations were targeted at the fluid in bulk phase and few study so far has been found to calculate the free energy of mixing and solubility parameter in nanopores.

In this study, the analytical formulations of the confined fluid free energy of mixing and solubility parameter at nanometer scale are proposed thermodynamically on a basis of the nanoscale-extended EOS in Chapter 3. Moreover, the conditions and characteristics of the fluid miscibility in nanopores are specifically studied by means of the thermodynamic derivations and quantitative calculations of the free energy of mixing and solubility parameter. Finally, the improved EOS model with the modified correlations is applied to calculate the miscibility-associated quantities of three mixing fluids, which are compared
with and validated by the literature results.

6.2 Materials

Pure CO₂, N₂, and a series of alkanes from C₁–C₁₀ are used, whose critical properties (i.e., temperature, pressure, and volume), van der Waals EOS constants, and Lennard-Jones potential parameters are summarized (Mansoori and Ali, 1974; Whitson and Brule, 2000; Yu and Gao, 2000) and listed in Table 3.1. In addition, as three hydrocarbon mixture systems, a ternary mixture of 4.53 mol.% n-C₄H₁₀ + 15.47 mol.% i-C₄H₁₀ + 80.00 mol.% C₈H₁₈ (Wang et al., 2014) and a live light crude oil (i.e., oil B) (Teklu et al., 2014b) are applied to study the miscibility of the mixture fluids. The compositional analyses of the ternary HC mixture and live oil systems as well as the detailed experimental set-up and procedures for preparing the oil samples were specifically introduced in the literature (Zhang and Gu, 2016a, 2016b, 2015).

6.3 Methods

In chemical engineering, to form a miscible blend, the free energy of mixing \( \Delta G \leq 0 \) and its second derivative with respect to the composition (i.e., solvent concentration) \( \frac{\partial^2 \Delta G}{\partial \phi^2} > 0 \) should be concurrently satisfied (Xavier et al., 2016),

\[
\Delta G = \Delta H - T \Delta S
\]  

(6.1)

where \( \Delta H \) is the enthalpy of mixing and \( \Delta S \) is the entropy of mixing. The enthalpy of mixing is defined as \( H = U - (PV) = U + PV \), the differentiation of which is shown as,

\[
dH = dU + dPV
\]  

(6.2)

Assuming that the work is only conducted in the radial direction and the pressure is
constant in the first order (e.g., liquid–vapour system) phase transition, the corresponding enthalpy of mixing is,

\[ \Delta H = H_g - H_l = (U_g - U_l) + P_i (V_g - V_l) \]  \hspace{1cm} (6.3)

Given that \( dU = TdS - PdV \) and the generalized Maxwell relationship of \( \frac{\partial S}{\partial V} = \frac{\partial P}{\partial T} \) \(_T\) (Gibbs, 1961),

\[ \frac{\partial U}{\partial V} = T \frac{\partial S}{\partial V} \big|_T - P_i = T \frac{\partial P}{\partial T} \big|_V - P_i \]  \hspace{1cm} (6.4)

Substituting Eq. (3.6b) into Eq. (6.4) to be,

\[ U = U_0 - \frac{N^2}{V^2} [a - 2\varepsilon\sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)] \]  \hspace{1cm} (6.5)

where \( U_0 \) is the internal energy of the ideal gas (Verdier and Andersen, 2005). The enthalpy of mixing \( \Delta H \) can be obtained by means of Eqs. (6.3) and (6.5),

\[ \Delta H = [a - 2\varepsilon\sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)] \left[ -\frac{N^2}{V_g} + \frac{N^2}{V_1} - \frac{N^2}{V_2} (V_g - V_1) \right] + \left( \frac{NkT}{V - Nb} \right) (V_g - V_1) \]  \hspace{1cm} (6.6)

Since \( T\Delta S = \Delta H - V\Delta P \), so

\[ \Delta G = \Delta H - T\Delta S = \Delta H - (\Delta H - V\Delta P) = V\Delta P = V(P_g - P_l) \]  \hspace{1cm} (6.7)

The free energy of mixing in bulk phase and nanopores can be expressed by substituting the conventional vdW-EOS and Eq. (2.6b) into Eq. (6.7),

\[ \Delta G_{BP} = a \left( \frac{VN^2}{V_g^2} + \frac{VN^2}{V_1^2} \right) + RT \left( \frac{V}{V_g - Nb} - \frac{V}{V_1 - Nb} \right) \]  \hspace{1cm} \text{bulk phase} \hspace{1cm} (6.8a)

\[ \Delta G_{NP} = [a - 2\varepsilon\sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)] \left( -\frac{VN^2}{V_g^2} + \frac{VN^2}{V_1^2} \right) + RT \left( \frac{V}{V_g - Nb} - \frac{V}{V_1 - Nb} \right) \]  \hspace{1cm} \text{nanopores} \hspace{1cm} (6.8b)

The effect of the pore radius on the free energy of mixing (miscibility) can be obtained by subtracting Eqs. (6.8a) and (6.8b),
\[ \Delta G_{\text{NP-BP}} = -2\varepsilon \sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right) \left( -\frac{VN^2}{V^2} + \frac{VN^2}{V^2_i} \right) \] (6.9)

Eq. (6.9) can be used to quantify the degree of the miscibility at a fixed feed ratio of gas to liquid.

In addition, a parameter was introduced to describe a solvent affinity to a solute, which was named as solubility parameter by Hildebrand (Hildebrand, 1936). The Hildebrand solubility parameter is a numerical value and derived from the cohesive energy density of the solvent. As aforementioned that for the substances without polar and hydrogen-bonding effect, such as light hydrocarbons, the values of the one-component Hildebrand solubility parameter almost equal to those of the three-component Hansen solubility parameters (Hansen, 1969). Thus the Hildebrand solubility parameter is used in this study for brevity, which was defined by Hildebrand et al. in 1950 as (Hildebrand, 1936),

\[ \delta = \left( \frac{\Delta E}{V} \right)^{1/2} = \left( \frac{\Delta U}{V} \right)^{1/2} \] (6.10)

where \( \delta \) denotes the Hildebrand solubility parameter, \( \Delta E \) means the cohesive energy, and \( V \) is the molar volume. The solubility parameters in bulk phase and nanopores can be calculated by substituting the conventional vdW-EOS and Eq. (6.5) into Eq. (6.10),

\[ \delta_{\text{BP}} = \left( \frac{aN^2}{v^2} \right)^{1/2} \text{ bulk phase} \] (6.11a)

\[ \delta_{\text{NP}} = \left[ \frac{aN^2 - 2N^2 \varepsilon \sigma^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right)}{v^2} \right]^{1/2} \text{ nanopores} \] (6.11b)

The difference of solubility parameters for different components is regarded as an important indication of the miscibility (Zhang et al., 2018b). More specifically, the smaller difference of solubility parameters of two components, the more easily they become
miscible. Furthermore, the effect of the pore radius on the solubility parameter (miscibility) can be obtained by subtracting Eqs. (6.11a) and (6.11b),

\[
\delta_{NP,BP} = \left[ -2\varepsilon \sigma^3 \frac{c_1 + c_2}{A} \frac{1}{\sqrt{v}} \right]^{1/2}
\] (6.12)

### 6.4 Results and discussion

#### 6.4.1 Miscibility of confined fluids

The free energies of mixing of CO\textsubscript{2}, N\textsubscript{2}, C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3}, i- and n-C\textsubscript{4} with C\textsubscript{8} at different pore radii are calculated from Eq. (6.9) and plotted in Figure 6.1a. Overall, the free energies of mixing become more negative with the reducing pore radius starting from 100 nm to 0.5 nm (a major reduction initiates from 10 nm). The more negative the free energy value is considered to represent a better miscible state (Xavier et al., 2016). It is found that the intermediate hydrocarbons (e.g., C\textsubscript{2}, C\textsubscript{3}, i- and n-C\textsubscript{4}) become more easily miscible with the liquid C\textsubscript{8} either in bulk phase or nanopores in comparison with the lean gas (e.g., N\textsubscript{2} and CH\textsubscript{4}). Furthermore, for alkanes, the miscible state becomes more easily to be achieved with the reduction of the pore radius for the system having the similar liquid and gas properties (e.g., molecular weight or structure). It should be noted from Figure 6.1a that the free energy of mixing starts to increase and the miscibility becomes harder to be reached once the pore radius is smaller than 0.5 nm. It is because the molecular diameter of C\textsubscript{8}H\textsubscript{18} is around 1 nm (Zhang and Gu, 2016b) so that only one C\textsubscript{8}H\textsubscript{18} molecule can be transported at the \( r_p = 0.5 \) nm (\( d_p = 1 \) nm). Obviously, a necessary condition for the fluid miscibility
Figure 6.1a Calculated (a1) free energy of mixing of CO\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, i- and n-C\textsubscript{4}H\textsubscript{10}, with the liquid phase of C\textsubscript{8}H\textsubscript{18} at different pore radii and (a2) molecular structure and diameter of C\textsubscript{8}H\textsubscript{18} from the predictive algorithm of B3LYP/6-31G* (Zhang and Gu, 2016b).
Figure 6.1b Calculated differences of solubility parameters of CO₂, N₂, CO₂, N₂, CH₄, C₂H₆, C₃H₈, i- and n-C₄H₁₀ with the liquid phase of C₈H₁₈ at different pore radii.
development is that both liquid and gas molecules can flow freely in the porous medium.

Figure 6.1b shows the differences of calculated solubility parameters ($\Delta \delta$) for CO$_2$, N$_2$, C$_1$, C$_2$, C$_3$, i- and n-C$_4$ with liquid C$_8$ at different pore radii, which share a similar pattern with the free energies of mixing that $\Delta \delta$ decreases with the reduction of the pore radius to $r_p = 0.5$ nm ($d_p = 1$ nm) and starts to increase afterwards. In general, the properties of liquid and gas phases become more similar and the fluid miscibility is more easily to be achieved with a smaller $\Delta \delta$ (Zhang et al., 2018b). Thus a similar conclusion is drawn from Figure 6.1a that the intermediate hydrocarbons are more miscible while the lean gas are less miscible with liquid C$_8$. The similar-property system is more sensitive to the variation of the pore radius and more easily to develop the miscibility with the reduction of the pore radius. Therefore, the increasing confinement effect from the reduction of the pore radius contributes to the miscibility of the liquid and gas phases. However, a bottom limit exists for the pore radius reduction, i.e., the molecular diameter of a single liquid molecule, which is the necessary condition for the miscibility development. The miscible state is contributed with the pore radius reduction when the pore radius is larger than the molecular diameter of the single liquid molecule. Otherwise, the miscible state will never be reached.

6.4.2 Case study

The modified EOS model with the improved correlations for predicting the shifts of critical temperature and pressure is applied to calculate the MMPs of the live light crude oil B and P–CO$_2$ systems in nanopores, which is an extension from the above-mentioned pure component to mixture systems. In Figure 6.2, the literature recorded (Teklu et al., 2014b) and calculated bubble point pressures and MMPs of the live light crude oil B and
Figure 6.2 Recorded (Teklu et al., 2014b) and calculated bubble point pressure ($P_b$) and minimum miscibility pressures (MMPs) of the live light crude oil B and P–CO$_2$ systems at the pore radii of 4–1,000 nm from the modified equation of state and diminishing interface method (Zhang et al., 2017b).
P–CO₂ systems versus the pore radius are plotted. The calculated bubble point pressures agree well with the recorded results at the same conditions in the literature (Teklu et al., 2014b). Both the bubble point pressure and MMPs are decreased with the reduction of the pore radius, especially when the pore radius is smaller than 100 nm. These findings are in good agreement with the literature results (Zhang et al., 2017b). On the other hand, the modified EOS model considering the both shifts of critical properties and capillary pressure presents a similar overall phase behaviour and miscibility pattern from the improved vdW-EOS in this study, which only takes into account the shifts of critical properties. It means that the shifts of critical properties are more important and dominate factors which affect the phase behaviour and miscibility changes from bulk phase to nanopores.

6.5 Summary

In this chapter, thermodynamic miscibility of confined pure and mixing fluids in nanopores are specifically studied. The thermodynamic free energy of mixing and solubility parameter are derived, quantitatively calculated, and applied to study the conditions and characteristics of the fluid miscibility in nanopores. The miscibility development of liquid–gas system is contributed with the reduction of the pore radius. The intermediate hydrocarbons (e.g., C₂, C₃, i- and n-C₄) perform better to be miscible with the liquid C₈ in comparison with the lean gas (e.g., N₂ and C₁). The molecular diameter of the single liquid molecule is determined to be the bottom limit for the pore radius reduction, above which the liquid–gas miscibility can be reached and improved by reducing the pore radius. Otherwise, the miscible state will never be reached. Finally, the proposed model has been proven to calculate the miscibility of confined pure and mixing fluids, even some high carbon number hydrocarbons, in an accurate and efficient manner.
CHAPTER 7  EXPERIMENTAL NANOFUIDICS

7.1  Introduction

Static phase behavior of the confined CO₂–tight fluids drastically change even in qualitative views under the strong confinements when the pore radius reduces to the nanometer scale and be comparable to the molecular size in tight reservoirs (Wu et al., 2017; Zarragoicoechea and Kuz, 2002; Zhang et al., 2018a). More importantly, such substantial changes of the phase behavior and fluid flow exert huge effects on the tight geological structure and formation physical properties, which may be detrimental to the CO₂ enhanced oil recovery (EOR) and even post-production sequestration processes in tight reservoirs (Dai et al., 2016; Middleton et al., 2015). Meanwhile, most classical experimental apparatus were restricted to the bulk phase and theoretical approaches are incapable of modeling the complex confinements, intermolecular interactions, or pore-size distribution (PSD) in confined porous media (Li et al., 2011, 2009). Thus, the static phase behavior of CO₂ EOR processes in tight reservoirs remain unclear.

At the current stage, few laboratory experiments are available in the public domain to investigate the confined fluids at the nanometer scale because of the high requirements of measurement precisions, observation/imaging systems, and associated costs (Bao et al., 2017a; Molla and Mostowfi, 2017; Zhong et al., 2016). Most existing studies, at the molecular scale, are mainly conducted theoretically, which include the equation of state (EOS) (Dall’Acqua et al., 2017; Yang and Lee, 1952), density functional theory (DFT) (Huang et al., 2015; Qin et al., 2018), Kelvin equation (Evans, 1990; Peterson and Gubbins, 1987), and molecular simulation (MS) (Hummer et al., 2001; Naguib et al., 2004). On a
basis of the above-mentioned experimental and theoretical approaches, several typical static phase changes have been revealed. More specifically, the bubble-point pressure of a confined mixing hydrocarbons was found to be significantly decreased while the upper dew-point pressure increased and lower dew-point pressure decreased with enhanced confinement effects (Dong et al., 2016; Salahshoor et al., 2017; Teklu et al., 2014b). Furthermore, the critical temperature and pressure of the confined fluids were concluded to shift under the strong confinements at the nanometer scale (Islam et al., 2015; Zarragoicoechea and Kuz, 2004). Continuous and discontinuous condensations and evaporations were observed in the nanopores due to the liquid bridging and lower initial liquid saturation pressures (Duan et al., 2012; Li et al., 2017; Zhong et al., 2016). However, in the experiment, most experimental apparatus for the nanometer scale are optically inaccessible so that the static phase behavior cannot be directly observed. Some published observable nanofluidic systems cannot tolerate high temperatures or pressures (Ally et al., 2016; Bao et al., 2017b; Krummel et al., 2013); in the theory, the simple and accurate EOSs are preferred because the other theoretical approaches are time-consuming for their intensive mathematical formulations and computational frameworks (Zhang et al., 2018a). Nevertheless, the complex confinement effects and their associated phenomena cannot be fully incorporated into the existing EOSs.

Another important issue is that most existing experimental and theoretical models use a single pore size to simulate the confinement effects on the fluid static behavior (Jin et al., 2017; Kowalczyk et al., 2008). The single-scale pores size is an ideal case but cannot be applicable for some practical applications, such as the unconventional oil/gas recovery from the tight formations, where at least dual-scale or even multi-scale micro/nanopores
coexist (L. Wang et al., 2016). Thus, to effectively simulate the dual/multi-scale micro/nanopores in the laboratory experiments and include it into the theoretical approaches is another challenge.

Here, static phase behavior of confined binary CO$_2$ mixtures in the dual-scale nanopores are experimentally and theoretically studied. A total of ten tests for two different kinds of experiments, constant composition expansion (CCE) and pressure–temperature curve measurements, of the confined CO$_2$–C$_{10}$ or C$_{10}$ fluids were conducted through a self-manufactured nanofluidic system at different conditions. Moreover, a generalized EOS including the comprehensive confinement and PSD effects is developed and applied to calculate the vapor–liquid equilibrium (VLE). In addition, the temperature and feed gas to liquid ratio (FGLR) effects on the fluid static behaviour are evaluated. All calculated data at the nanometer scale are validated by the experimentally measured results. In this study, for the first time, the model combines the mechanic statistics with the conventional thermodynamic EOS by incorporating the confinements, intermolecular interactions and the pore size distribution function. Also, the calculated phase behavior of confined CO$_2$ fluids are effectively verified through a series nanofluidics tests. The tight confinements and their associated effects on the static CO$_2$ behavior are clearly evaluated, on the basis of which the foundations of more general application pertaining to CO$_2$ EOR and post-production sequestration processes are elucidated.

7.2 Method

Experimental

**Materials** In this study, pure CO$_2$ and $n$-decane, whose critical properties (i.e., temperature, pressure, and volume), equation of state (EOS) constants, and Lennard-Jones
potential parameters are summarized (Whitson and Brule, 2000; Yu and Gao, 2000) and listed in Table S1, with respective purities of 99.998 and 99.0% are used and reconstituted to be the gas-saturated fluids. The detailed experimental set-up and procedures for preparing the gas-saturated fluids were specifically introduced in the literature (Zhang and Gu, 2015).

A high-pressure and high-temperature nanofluidic apparatus is self-manufactured and used, whose maximum operating pressure and temperature are equal to 40 MPa and 150 °C, respectively. The major component of the nanofluidic apparatus is a hybrid micro- and nanofluidic chip, which was fabricated through deep reactive ion etching of silicon and anodically bonded to glass. The detailed chip fabrication information are recorded in Appendix III. The chip consists of six micro-channels with a dimension of 20 μm (width) × 10 μm (depth) and eleven nano-channels with a dimension of 10 μm (width) × 100 nm (depth), whose schematic diagram is shown in Figure 7.1. It should be noted that the micro-channels are perpendicularly connected to the nano-channels to avoid direct injections (i.e., increase fluid injectivities) and dampen pressure fluctuations. In addition, two high-pressure cylinders and three high pressure pumps (100DX, ISCO Inc., USA) were used to hold and generate the fluid. All images were captured by a high-speed 4K camera coupled with an inverted optical microscope from Olympus and processed through a MATLAB image processing code.

Experimental procedures Some preliminary tests, such as the pressure leakage and fluid injection tests, were conducted before each set of experiments. All tubing, valves, cylinders, and pumps were cleaned thoroughly before connecting to the nanofluidic apparatus. Take the constant composition expansion (CCE) test of the CO₂-saturated
Figure 7.1a Schematic diagram of the self-fabricated hybrid micro- and nano-fluidic chip.
**Figure 7.1b** Schematic diagram of the fabrication process on the cross-sectional perspective.
$n$-decane fluids at the ambient temperature as an example. More specifically, the assembled system was initially vacuumed at $-100$ kPa for 2 hours to minimize the residual air in the system. Then, the reconstituted research-grade CO$_2$-saturated $n$-decane fluids were filled the system at $P = 8.5$ MPa (bubble-point pressure approximately equals to 4.2 MPa in bulk phase at the ambient temperature) and the fluid system reached the equilibrium state after 1 hour. Afterwards, the pressure was decreased from 8.5 MPa in steps of 0.2 MPa until the target pressure was reached. At least 30 mins were used for each step to ensure the system to reach the equilibrium and another 30 mins were used to detect and capture any phenomena. The first bubble was instantaneously captured when the pressure inside the channels dropped below its bubble-point pressure ($P_b$). The above-mentioned processes are isothermal because the temperature was fixed throughout the tests. For the isobaric experiments, the pressure was kept at some pressure moderately higher than the $P_b$ at the initial temperature and the temperature was increased from the lower to higher temperatures. All temperatures and pressures were detected and recorded during each test, whose experimental errors were equal to $\pm 0.01$ kPa and $\pm 0.1$ °C, respectively. Please note that the pressure–temperature measurements share similar procedures with the CCE experiments but with different FGLRs.

**Theoretical**

The VLE in nanopores are affected by the joint confinement and PSD effects concurrently, the latter of which usually induces the sequence of phase changes and membrane phenomena. In this study, the PSD effects are incorporated into a generalized nanoscale-extended EOS, which considers the effects of pore size, molecule–molecule and molecule–wall interactions, to calculate the phase properties of the confined fluids in dual-
scale nanopores. Figure 4.7 shows the schematic diagrams of the nanopore network model, configuration energy, and intermolecular potentials in nanopores. The detailed derivations for the generalized EOS are specified in Chapter 4, whose analytical formulation is shown as follows,

\[
P(N,V,T) = \frac{RT}{V - Nb} - \frac{N^2}{V^2} \left[ a - 2\varepsilon_{LJ}\sigma_{LJ}^3 \left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right) \right] - \frac{b\theta}{V^2} \left( 1 - \frac{b}{V} \right)^{\theta-1} \left( 1 - F_{pr} \right) \left[ RT \left( 1 - e^{-N_s\varepsilon_{sw}/RT} \right) - N_A\varepsilon_{sw} \right]
\]

(7.1)

where \( R \) is the universal gas constant, \( a \) and \( b \) are the EOS constants, \( \varepsilon_{LJ} \) is the molecule–molecule Lennard–Jones energy parameter, \( \sigma_{LJ} \) is the molecule–molecule Lennard–Jones size parameter, \( c_1 = 3.5622, c_2 = -0.6649 \) (Zhang et al., 2018a), \( F_{pr} \) is the fraction of the random distributed fluid molecules in the square-well region of the pores, \( \Theta \) is the geometric term, \( N_A \) is the Avogadro constant, and \( \varepsilon_{sw} \) is the molecule–wall square-well energy parameter.

The sequential phase changes and membrane phenomena representing the PSD effects are incorporated into the modified EOS. Physically, the sequential phase changes are directly caused by the strong confinement effects so that they instantaneously occur, which are followed by the compositional differential induced membrane phenomena. The schematic diagram of the sequential phase changes in the dual-scale nanopores is shown in Figure 7.2. In brief, considering the sequential phase changes, the vapor faction (\( \beta \)) can be updated (L. Wang et al., 2016),

\[
\beta = \frac{V_{LS}}{V_{LS} + V_{SS}}
\]

(7.2)
Figure 7.2 (a) Schematic diagram of the sequential phase changes in the dual-scale nanopores and (b) Captured images of each stage from the nanofluidic experiments.
where $V_{LS}$ and $V_{SS}$ are the volumes of the large size (LS) and small size (SS) nanopores, respectively. The compositions of the remaining fluids change accordingly due to the sequential phase changes, which subsequently results in the membrane phenomena through two different-size nanopores. At equilibrium, the fugacity of the light components $x$ should be identical while the fugacity of the heavy component $y$ cannot be equivalent in the two nanopores due to the membrane phenomena, so (Zhu et al., 2015),

$$f^y_{x1} = f^L_{x2}$$  \hspace{1cm} (7.3a)

$$f^y_{y1} = \frac{f^L_{x2}}{1 - w_f}$$  \hspace{1cm} (7.3b)

where $w_f$ is the membrane efficiency. Since the nanopore systems are closed, the changes of the number moles for components $x$ and $y$ should be zero at the equilibrium state,

$$|\Delta n_{x1}| = |\Delta n_{x2}|, \quad |\Delta n_{y1}| \neq |\Delta n_{y2}|$$  \hspace{1cm} (7.4)

In order to satisfy Eqs. 7.3 and 7.4 concurrently, the composition of the LS nanopores can be updated,

$$z'_{x1} = \frac{n_{x1} + \Delta n_{x1}}{n_{x1} + \Delta n_{x1} + n_{y1} + \Delta n_{y1}}$$  \hspace{1cm} (7.5a)

$$z'_{y1} = 1 - z'_{x1}$$  \hspace{1cm} (7.5b)

The modified VLE calculations based on the modified EOS (i.e., Eq. (7.1)) coupled with the PSD effects (i.e., sequential phase changes and membrane phenomena) require a series of iterative computation through, for example, the Newton–Raphson method, whose detailed procedures are also specified in Chapter 2.
7.3 Results and discussion

In this study, pure CO$_2$ and n-decane ($C_{10}$) are used for a total of ten tests for two different laboratory experiments in bulk phase and self-fabricated nanofluidic system at different conditions. More specifically, in experimental work, four tests of the CCE experiment for the CO$_2$-saturated $C_{10}$ at the FGLR of 0.5:0.5 in mole fraction and temperatures of $T = 25.0$ and 53.0 °C in bulk phase and micro/nano-channels and six tests of the pressure–temperature curve measurements for the CO$_2$-saturated $C_{10}$ at $T = 25.0$ °C and the FGLRs of 0.25:0.75, 0.5:0.5, and 0.75:0.25 in bulk phase and micro/nano-channels are conducted. In theoretical work, a generalized EOS for the bulk phase and nanoscale calculations is developed, which is applied to calculate the VLE or static behavior of confined fluids by including the confinement and PSD effects concurrently.

Some previous studies have validated that the fluid phase behavior experience drastic changes when the pore size reduces to the nanometer scale (Dong et al., 2016; Wu et al., 2018; Zhang et al., 2018a). In this study, the pressure–volume and pressure–temperature curves of the confined CO$_2$–$C_{10}$ fluids in dual-scale nanopores at different temperatures and FGLRs are experimentally measured, which are compared with the measured and calculated bulk phase results in Figures 7.3 and 7.4. It is found from the figures that all the measured pressure–volume and pressure–temperature curves in nanopores are lower than those in bulk phase, which means that the saturation pressures ($P_{sat}$) of the CO$_2$–$C_{10}$ fluids are much depressed under the strong confinement effects in nanopores. More precisely, in Figures 7.3a and b, the measured $P_{sat}$ are found to decrease from 4231 kPa in bulk phase to 3800 kPa in nanopores and from 6362 kPa in bulk phase to 5900 kPa in nanopores at the
Figure 7.3a Measured and calculated pressure–volume curves of the CO$_2$–C$_{10}$ fluid in bulk phase and dual-scale nanopores at the temperature of 25.0 °C.
Figure 7.3b Measured and calculated pressure–volume curves of the CO$_2$–C$_{10}$ fluid in bulk phase and dual-scale nanopores at the temperature of 53.0 °C.
Figure 7.4a Measured and calculated pressure–temperature curves of the CO$_2$–C$_{10}$ fluid in bulk phase and dual-scale nanopores at the feed gas to liquid ratio (FGLR) of 0.5:0.5 in mole fraction ($a >> P_b$ in bulk phase; $P_b$ in nanopores $< b < P_b$ in bulk phase; $c \approx$ or $< P_b$ in nanopores; $d << P_b$ in nanopores).
Figure 7.4b Measured and calculated pressure–temperature curves of the CO$_2$–C$_{10}$ fluid in bulk phase and dual-scale nanopores at the feed gas to liquid ratio (FGLR) of 0.75:0.25.
Figure 7.4c Measured and calculated pressure–temperature curves of the CO₂–C₁₀ fluid in bulk phase and dual-scale nanopores at the feed gas to liquid ratio (FGLR) of 0.25:0.75 in mole fraction.
FGLR of 0.5:0.5 in mole fraction and $T = 25.0$ and 53.0 °C, respectively. In comparison with the bulk phase cases, the percentage average absolute deviations (AAD%) of the reduced saturation pressures in nanopores are 10.19% at $T = 25.0$ °C and 7.26% at $T = 53.0$ °C. This phenomenon is also presented in Figures 7.4a–c, where the measured and calculated pressure–temperature curves of the confined CO$_2$–C$_{10}$ fluids in bulk phase and nanopores at the FGLRs of 0.5:0.5, 0.75:0.25, and 0.25:0.75 in mole fraction are shown. It is found at pressure $b$ in Figure 7.4a, which actually is lower than the $P_{\text{sat}}$ in bulk phase, that no gas bubble come out in the captured image. Gas bubble initiates and the fluids in the channel become slightly brighter at pressure $c$, which is the actual $P_{\text{sat}}$ in nanopores and equals to 3800 kPa. After that, more gas bubbles come out and occupy the channels as shown in pressure $d$ with further pressure reductions. Similar patterns are also obtained in the cases at the FGLRs of 0.75:0.25 and 0.25:0.75.

Under the strong confinements in nanopores, the PSD effects (i.e., the joint effects of sequential phase changes and membrane phenomena) included or not makes a big difference even in qualitative views. The PSD effects are directly observed from the captured videos of the nanofluidic experiments in this study. The evaporation and condensation processes for the confined CO$_2$–C$_{10}$ fluids in dual-scale micro/nano-channels were directly observed from the nanofluidic experiments. Please note that the pressure had been reduced to be below the saturation pressure and the temperature was kept constant throughout the tests. With the pressure reductions, gas bubbles firstly appear in the micro-channels and started to enter the nano-channels until all micro-channels have been filled. On the other hand, fluid condensations initiate in the nano-channels and spread to the micro-channels until all nano-channels are saturated with liquids by increasing the pressure.
Figures 7.3 and 7.4 show the calculated pressure–volume and pressure–temperature curves in nanopores without and with PSD effects and their differences are obvious. Overall, the calculated data with the PSD effects agree well with the measured results at any conditions while the calculated ones without the PSD effects are deviated to different extents. More specifically, the calculated CO$_2$–C$_{10}$ $P_{\text{sat}}$ in Figure 7.3 are 4050 and 3897 kPa at $T = 25.0$ °C and 6083 and 5955 kPa at $T = 53.0$ °C without and with including the PSD effects, respectively. Given that the measured saturation pressures in nanopores are 3800 and 5900 kPa, the AAD% of the calculated data without and with the PSD effects are 6.58 and 2.55% at $T = 25.0$ °C and 3.10 and 0.93% at $T = 53.0$ °C, respectively. Furthermore, Figures 7.4a–c show that the calculated $P_{\text{sat}}$ without including the PSD effects are closer to the calculated bulk $P_{\text{sat}}$ and always higher than those with the PSD effects at different temperatures and FGLRs. More quantitative phase properties in nanopores are calculated without and with the PSD effects, which are summarized and compared with the measured results (where the liquid and vapor fractions were measured while other properties were calculated based on the measured liquid and vapor fractions) in Table 7.1. It is clearly seen that the calculated data with the PSD effects provide more accurate results for all phase properties. In comparison with the measured and calculated data including the PSD effects, without including the PSD effects results in higher values in terms of the liquid fractions, interfacial tensions, vapor phase density and viscosity but lower values in terms of the capillary pressures in micro and nano-channels. They are attributed to the neglects of the sequential phase changes (i.e., vapor phase appears in the larger channel first) and membrane phenomena (i.e., heavier components trapped and cannot transport through dual-scale channels) without including the PSD effects. Thus, it is concluded that in the
Table 7.1
Measured and calculated pressure–volume–temperature data from the generalized equation of state for the CO$_2$–C$_{10}$ system in the micro-channel of 20 × 10 μm and nano-channel of 10 μm × 100 nm (W × H) at (a) constant pressure and (b) constant temperature.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before flash experiment</th>
<th>After flash experiment</th>
<th>After flash calculation (without PSD effects)</th>
<th>AAD$^e$ %</th>
<th>After flash calculation (with PSD effects)</th>
<th>AAD$^e$ %</th>
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<tr>
<td>Temperature (°C)</td>
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<td>53.0</td>
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<td></td>
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<td></td>
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<tr>
<td>Pressure (kPa)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid (CO$<em>2$–C$</em>{10}$, mol.%)</td>
<td>50.00 50.00</td>
<td>38.02 61.98</td>
<td>42.33 57.67</td>
<td>9.14$^f$</td>
<td>39.50 60.50</td>
<td>3.14$^f$</td>
</tr>
<tr>
<td>Vapor (CO$<em>2$–C$</em>{10}$, mol.%)</td>
<td>0.00 0.00</td>
<td>73.66 26.34</td>
<td>75.92 24.08</td>
<td>5.82$^f$</td>
<td>74.11 25.89</td>
<td>1.16$^f$</td>
</tr>
<tr>
<td>Liquid fraction (mol.%)</td>
<td>100.00</td>
<td>69.30 73.65</td>
<td>6.31 70.23</td>
<td>1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vapor fraction (mol.%)</td>
<td>0.00</td>
<td>30.70 26.35</td>
<td>14.23 29.77</td>
<td>3.09</td>
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<td></td>
</tr>
<tr>
<td>IFT (mJ/m$^2$)</td>
<td>– 13.03</td>
<td>14.22 9.13</td>
<td>13.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho$ (kg/m$^3$)</td>
<td>811.57$^a$ –</td>
<td>788.34$^a$ 155.42$^b$</td>
<td>742.13$^a$ 189.62$^b$</td>
<td>13.93$^f$</td>
<td>772.32$^a$ 160.21$^b$</td>
<td>2.56$^f$</td>
</tr>
<tr>
<td>$\mu$ (cP)</td>
<td>0.3649$^a$ –</td>
<td>0.3545$^a$ 0.0218$^b$</td>
<td>0.3033$^a$ 0.0634$^b$</td>
<td>102.63$^f$</td>
<td>0.3327$^a$ 0.0306$^b$</td>
<td>23.26$^f$</td>
</tr>
<tr>
<td>$P_{\text{cap}}$ (kPa)</td>
<td>–</td>
<td>4.98$^c$ 169.18$^d$</td>
<td>3.55$^c$ 121.34$^d$</td>
<td>28.50$^f$</td>
<td>4.22$^c$ 150.51$^d$</td>
<td>13.15$^f$</td>
</tr>
</tbody>
</table>

(b) constant temperature case

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before flash experiment</th>
<th>8500</th>
<th>After flash experiment</th>
<th>3600</th>
<th>After flash calculation (without PSD effects)</th>
<th>AAD$^e$ %</th>
<th>After flash calculation (with PSD effects)</th>
<th>AAD$^e$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>21.0</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (kPa)</td>
<td>8500 3600</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid (CO$<em>2$–C$</em>{10}$, mol.%)</td>
<td>50.00 50.00</td>
<td>40.51 59.49</td>
<td>36.78 63.22</td>
<td>7.14$^f$</td>
<td>39.03 60.97</td>
<td>3.07$^f$</td>
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<td></td>
</tr>
<tr>
<td>Vapor (CO$<em>2$–C$</em>{10}$, mol.%)</td>
<td>0.00 0.00</td>
<td>82.97 17.03</td>
<td>85.82 14.18</td>
<td>10.09$^f$</td>
<td>83.77 16.23</td>
<td>2.83$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid fraction (mol.%)</td>
<td>100.00</td>
<td>82.97 17.03</td>
<td>42.04 9.79</td>
<td>4.52</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Vapor fraction (mol.%)</td>
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<td>61.70 57.96</td>
<td>6.08 59.98</td>
<td>2.80</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>IFT (mJ/m$^2$)</td>
<td>–</td>
<td>11.38</td>
<td>13.76 20.91</td>
<td>12.07</td>
<td>6.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\rho$ (kg/m$^3$)</td>
<td>779.38$^a$ –</td>
<td>833.02$^a$ 156.97$^b$</td>
<td>797.35$^a$ 171.33$^b$</td>
<td>6.72$^f$</td>
<td>827.60$^a$ 161.03$^b$</td>
<td>1.62$^f$</td>
<td></td>
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</tr>
<tr>
<td>$\mu$ (cP)</td>
<td>0.3395$^a$ –</td>
<td>0.3801$^a$ 0.0267$^b$</td>
<td>0.3361$^a$ 0.0421$^b$</td>
<td>34.63$^f$</td>
<td>0.3502$^a$ 0.03778$^b$</td>
<td>24.68$^f$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_{\text{cap}}$ (kPa)</td>
<td>–</td>
<td>3.87$^c$ 115.55$^d$</td>
<td>2.98$^c$ 97.66$^d$</td>
<td>19.24$^f$</td>
<td>3.54$^c$ 107.22$^d$</td>
<td>7.87$^f$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:
- a: liquid phase; b: vapor phase; c: micro-channel; d: nano-channel; e: calculated percentage absolute average deviations f: average AAD% of the two values.
dual or multi-scale nanopores, any phase calculations without including the PSD effects can be incomplete in physics and inaccurate in results.

In addition to the above-mentioned confinement and PSD effects, the temperature and FGLR affect the phase behavior of confined fluids in bulk phase and nanopores. A commonly apparent phenomenon from Figures 7.3 and 7.4 is that higher temperatures increase the saturation pressures in bulk phase and nanopores. Figures 7.4a–c even indicate linear relationships between the temperatures and measured saturation pressures within temperatures of $T = 15–70 \, ^\circ\text{C}$ in bulk phase and nanopores, whose specific linear regression equations are listed as follows,

FGLR = 0.5:0.5:

\[
\text{Bulk phase} \quad P = 75.9392T + 2397.5576 \quad (R^2 = 0.9976) \quad (7.6a)
\]

\[
\text{Nanopores} \quad P = 78.7155T + 1774.0894 \quad (R^2 = 0.9967) \quad (7.6b)
\]

FGLR = 0.75:0.25:

\[
\text{Bulk phase} \quad P = 139.7470T + 2394.8013 \quad (R^2 = 0.9950) \quad (7.7a)
\]

\[
\text{Nanopores} \quad P = 122.3296T + 2382.1884 \quad (R^2 = 0.9954) \quad (7.7b)
\]

FGLR = 0.25:0.75:

\[
\text{Bulk phase} \quad P = 31.0190T + 1284.2881 \quad (R^2 = 0.9997) \quad (7.8a)
\]

\[
\text{Nanopores} \quad P = 31.8588T + 899.1507 \quad (R^2 = 0.9982) \quad (7.8b)
\]

Moreover, the reduction rates of the pressures with respect to the volumes, especially for the first range of the pressure–volume curves, are increased with temperature increases, which means the gas come out more easily with temperature increases either in bulk phase or nanopores. This is mainly attributed to the reduced gas solubility with an increasing
temperature (Zhang et al., 2018e). The FGLR effects on the saturation pressure vs. temperature curves can be qualitatively reviewed from Figures 7.4a–c and quantitatively analyzed from the above-mentioned equations. Generally, more feed gas into the fluids (i.e., a higher FGLR) causes the saturation pressures to be more sensitive to the temperatures (i.e., saturation pressure increases faster with the unit temperature increase) in bulk phase and dual-scale nanopores. In summary, the effects of the temperature and FGLR on the phase behavior share similar manners in bulk phase and dual-scale nanopores.

### 7.4 Summary

In summary, static phase behavior of confined CO$_2$ fluids in dual-scale nanopores are experimentally and theoretically investigated. The static behavior are found to change drastically in the target dual-scale nanopores. More specifically, the measured saturation pressures of the confined CO$_2$–C$_{10}$ fluids reduce in 10.19% at $T = 25.0 \, ^\circ C$ and 7.26% at $T = 53.0 \, ^\circ C$ from bulk phase to the target nanometer scale. Furthermore, under the strong confinements, the PSD effects are necessary to be included in the dual/multi-scale nanopores. The calculated phase properties, i.e., the saturation pressures, liquid/vapor compositions and fractions, interfacial tensions, densities, viscosities, and capillary pressures, with including the PSD effects provide more accurate results in comparison with those without the PSD effects. In addition, the temperature and FGLR are specifically studied and their effects on the static phase behavior in nanopores share similar manners with the bulk phase cases. All calculations have been validated by the experimentally measured results. The specific experimental/calculation conditions target on the dual/multi-scale micro/nanoscale porous media, where the significant deviations from the bulk phase cases are mainly attributed to the confinement and PSD effects.
For the first time, the model combines the mechanic statistics with the conventional thermodynamic equation of state by incorporating the interaction potentials of molecule-molecule, molecule–wall of porous medium and the pore size distribution function. The new proposed numerical model illustrates the influences on the phase behavior for CO\textsubscript{2} EOR and sequestration processes from the different prospective of pore size and nanoscales. The generated phase behavior from the dual-pore size physical model have captured the sequential phase change for vaporization and condensation, and membrane phenomena of heavy hydrocarbon. Those experimental results will facilitate the detailed and deeper mechanisms’ explanations for describing onset of phase change occurrence at different sites of the porous medium from micro- and nanometer levels. The results from this study support the foundation of more general application pertaining to producing tight fluids and sequestrating CO\textsubscript{2} in tight reservoir characterization and exploration.
CHAPTER 8  CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

In this study, thermodynamic phase behavior and miscibility of confined fluids in nanopores have been comprehensively investigated. The major work and conclusions that can be drawn from this study are listed as follows:

1. A semi-analytical nanoscale-extended equation of state (EOS) coupled with two modified critical shift correlations is developed to accurately calculate the phase behavior of confined pure and mixing fluids in nanopores. Overall, the phase behavior in nanopores are substantially different from that in bulk phase. The critical temperature and pressure of confined fluids are decreased with the reduction of pore radius to

\[ \frac{\sigma}{r_p} = 0.1, \]

which dominate the changes of phase behaviour in comparison with the influences of the increased capillary pressure from bulk phase to nanopores.

2. Two new nanoscale-extended alpha functions, i.e., M-Soave and M-exponential, are developed analytically to calculate the phase and thermodynamic properties in bulk phase and nanopores coupled with a modified Soave–Redlich–Kwong EOS (SRK EOS). Another new method is proposed to determine the nanoscale acentric factors. The modified Soave and exponential-based alpha functions and their derivatives perform different but they are accurate in bulk phase and nanopores.

3. The pressure dependence of the equilibrium interfacial tensions (IFTs) of three different light crude oil–CO₂ systems is analyzed on the basis of the predicted equilibrium two-phase compositions. CO₂ dissolution accounts for 90% of the total compositional change in the mass-transfer process and the density difference is a key factor in the
parachor model for the IFT predictions, both of which are affected by the initial oil and gas compositions. The miscibility of the oil–pure/impure CO₂ system can be achieved at the initial gas mole fractions of > 0.70 and at certain threshold pressure.

4. Confined fluid IFTs in nanopores and their influential factors are studied on the basis of a new generalized EOS including the pore radius effect, intermolecular interactions, and wall effect coupled with the parachor model. The IFTs in bulk phase of the pure and mixing hydrocarbon (HC) systems are always higher than those in nanopores. The initial fluid composition and temperature exert strong effects while the feed gas to liquid ratios (FGLRs) have no effect on the confined IFTs. The IFTs are decreased by reducing the pore radius but keep constant at $\delta_p / r_p \geq 1.0$.

5. A new interfacial thickness-based method, the diminishing interface method (DIM), is developed to accurately determine the minimum miscibility pressures (MMPs) of light oil–CO₂ systems in bulk phase and nanopores. The MMP is determined by extrapolating the derivative of the interfacial thickness with respect to the pressure $(\partial \delta / \partial P)_T$ to zero. Physically, the interface between the light oil and CO₂ diminishes and the two-phase compositional change reaches its maximum at the determined MMP from the DIM.

6. A novel nanoscale-extended correlation is developed to calculate the MMPs for a wide range of dead and live tight oil–gas solvent systems in bulk phase and nanopores. A total of 40 commonly-used existing correlations are analyzed and reviewed. Compared to the existing correlations, the new correlation is found to provide the most accurate MMPs with an overall percentage average absolute deviation (AAD%) of 5.72% and maximum absolute deviation (MAD%) of 12.96% in bulk phase and AAD% of 6.91%
and MAD% of 13.66% in nanopores.

7. Thermodynamic miscibility of confined pure and mixing fluids in nanopores are studied based on the semi-analytical nanoscale-extended EOS. The liquid–gas miscibility is beneficial from the pore radius reduction and the intermediate hydrocarbons (e.g., C₂, C₃, i- and n-C₄) perform more miscible with the liquid C₈ in comparison with the lean gas (e.g., N₂ and CH₄). Moreover, the molecular diameter of single liquid molecule is determined to be the bottom limit, the pore radius above which is concluded as a necessary condition for the liquid–gas miscibility.

8. A nanofluidic system is developed to experimentally measure the static phase behavior of confined CO₂ fluids in dual-scale nanopores. More specifically, the measured saturation pressures of the confined CO₂–C₁₀ fluids reduce in 10.19% at \( T = 25.0 \) °C and 7.26% at \( T = 53.0 \) °C from bulk phase to the target nanometer scale. The calculated phase properties with including the pore-size distribution (PSD) effects provide more accurate results in comparison with those without the PSD effects.

8.2 Recommendations

1. The intrinsic mechanisms for some abnormal phenomena with respect to the phase behavior and miscibility of confined fluids in nanopores can be further analyzed.

2. Restrictions regarding the applicability of the model exist due to the applications of the empirical parameters. Hence, further work can be conducted with another potentials, cubic EOS, or empirical quantities to improve the model and better evaluate their effects on the confined fluid phase behaviour and miscibility in nanopores.

3. The multi-scale pore network should be incorporated into the theoretical and/or experimental methods in order to better model the actual porous media in the tight
formations.

4. More functional nanofluidic systems with higher temperature and pressure tolerances as well as different materials and scales are expected to be designed, manufactured and applied to better simulate the complex reservoir conditions.
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APPENDIX I

In this section, five empirical correlations, two semi-analytical or analytical methods (i.e., key tie line method and multiple-mixing cell algorithm), and two equation of state (EOS)-based methods are applied to calculate the minimum miscibility pressures (MMPs) of the Pembina dead and live oil–pure and impure CO₂ systems and the Bakken live oil–pure CO₂ system in bulk phase and nanopores at \( T_{\text{res}} = 53.0 \) and 116.1°C. The calculated MMPs are compared with the determined MMPs from the new diminishing interface method (DIM) and the measured MMPs from the slim-tube/coreflood tests (Zhang and Gu, 2015) and vanishing interfacial tension (VIT) technique (Zhang and Gu, 2016b) for the same oil–gas systems at the same conditions, which are summarized and listed in Tables A1.1a and b.

In petroleum industry, the empirical correlation is a relatively efficient and accurate way to estimate the MMPs (Emera and Sarma, 2005). In general, the empirical correlation takes into account the reservoir temperature, oil composition (e.g., molecular weight of \( C_7^+ \) fraction and mole fraction ratio of volatile to intermediate components), and gas composition (Emera and Sarma, 2005). Five correlations are used in this section, first, the original Alston correlation takes the following form (Alston et al., 1985),

\[
MMP = 8.78 \times 10^{-4} (1.8T_R + 32)^{1.06} (MW_{C5^+})^{1.78} (\frac{x_{\text{VOL}}}{x_{\text{INT}}})^{0.136}
\]  

(A1.1)

where \( T_R \) is the reservoir temperature; \( MW_{C5^+} \) is the molecular weight of \( C_5^+ \); \( x_{\text{VOL}} \) is the mole fraction of volatile components including N₂ and CH₄; and \( x_{\text{INT}} \) is the mole fraction of intermediate components including CO₂, H₂S, and C₂–C₄. Later, Li et al. modified the
original Alston correlation for estimating MMPs of dead and live oil–CO$_2$ systems as follows (Li et al., 2012),

$$MMP = 7.30991 \times 10^{-5} [\ln(1.87T_R + 32)]^{5.33647} [\ln(MW_{C_{1s}})]^{2.08836} (1 + \frac{x_{VOL}}{x_{INT}})^{2.01658 \times 10^4} \quad (A1.2)$$

In addition, Yuan et al. used an analytical theory from the EOS to generate the following correlation to calculate the MMPs for pure and impure CO$_2$ (Yuan et al., 2004),

$$MMP_{\text{pure}} = a_1 + a_2 MW_{C_{7+}} + a_3 x_{C_{1s+}} + (a_4 + a_5 MW_{C_{7+}} + a_6 \frac{x_{C_{1s+}}}{MW_{C_{7+}}}^2)T_R + (a_7 + a_8 MW_{C_{7+}} + a_9 MW_{C_{7+}} + a_{10} x_{C_{1s+}})T_R^2 \quad (A1.3)$$

$$\frac{MMP_{\text{imp}}}{MMP_{\text{pure}}} = 1 + m(y_{CO_2} - 100) \quad (A1.4)$$

$$m = a_1 + a_2 MW_{C_{7+}} + a_3 x_{C_{1s+}} + (a_4 + a_5 MW_{C_{7+}} + a_6 \frac{x_{C_{1s+}}}{MW_{C_{7+}}}^2)T_R + (a_7 + a_8 MW_{C_{7+}} + a_9 MW_{C_{7+}} + a_{10} x_{C_{1s+}})T_R^2$$

where $MMP_{\text{pure}}$ is the estimated MMP for pure CO$_2$ injection; $MMP_{\text{imp}}$ is the estimated MMP for impure CO$_2$ injection; $MW_{C_{7+}}$ is the molecular weight of $C_{7+}$; $x_{C_{2s}}$ is the mole fraction of $C_2$–$C_4$ in oil; $a_i$ is the empirical coefficient, $i = 1…10$; and $y_{CO_2}$ is the mole fraction of CO$_2$ in injection gas. Recently, two correlations are developed/modified to estimate the pure and impure CO$_2$ MMPs, first of which is the Shang correlation (Shang et al., 2014),

$$MMP = \exp\{[T_R^b + g] [\ln(MW_{C_{7+}})]^f + h(\exp(\frac{x_{VOL}}{x_{INT}}))^d + i(x_{C_{7+}})^j \} \quad (A1.5)$$

$$MMP = \exp\{a T_R^b E^c f^{x_{CO_2}} + D^m i^{x_{H_2}} j^{x_{CH}} (x_{C_{7+}})^d - g^{x_{H_2}} - h^{x_{C_2-C_1}} \} \quad (A1.6)$$

$$MMP = (a T_R^b + E^c D^f (\exp(x_{CO_2}))^g) (x_{C_{7+}})^d (h^{x_{H_2}} - i^{x_{C_2-C_1}} + j) + T_R^m \quad (A1.7)$$
\[ E = (MW_{C7+})^{x_{\text{mol}} / x_{\text{INT}}} \]

\[ D = \exp(x_{N_2}) \exp(x_{\text{CH}_4}) / \exp(x_{CO_2}) \]

Eqs. (A1.5)–(A1.7) are used to calculate the MMPs for pure CO₂, \( y_{CO_2} < 0.5 \), and \( y_{CO_2} > 0.5 \), respectively, where \( x_{C7+} \) is the mole fraction of \( C_{7+} \) in oil; \( x_{N_2} \), \( x_{\text{CH}_4} \), \( x_{\text{H}_2\text{S}} \), \( x_{\text{C2-C7}} \) is N₂, CH₄, H₂S, and C₂–C₇ mole fraction in injection gas; and \( a \), \( b \), \( c \), \( d \), \( f \), \( g \), \( h \), \( i \), \( j \), and \( m \) are empirical coefficients. In addition, Valluri et al. developed an optimized power law model as shown (Valluri et al., 2017),

\[ MMP = 0.3123 R^{0.9851} MW^{0.7421}_{C5+} \]  

(A1.8)

It is found from Table A1.1a that in comparison with the MMPs from the correlations, those from the DIM have the smallest absolute deviations (ADs) with the measured MMPs for all cases in bulk phase. The correlations seems to be insensitive to the oil/gas compositional change to different extents, plus some of them are only applicable for dead oil or pure CO₂ case. Also, all existing five correlations cannot be applied to estimate the MMPs in nanopores. It should be noted that no ADs for the results of the nanopore cases in Tables A1.1a and b since no experimentally measured MMPs for these oil–gas systems in nanopores.

In addition to the above-mentioned correlations, some semi-analytical or analytical methods are also used to calculate the MMPs (Shokir, 2007). More specifically, the key tie line (KTL) method (Orr Jr et al., 1993) and multiple-mixing cell (MMC) algorithm (Ahmadi and Johns, 2011) in the CMG Winprop module are applied in this study. Figure A1.1 shows the flow chart of the KLT method for calculating the MMP. In this method, the geometry of the key tie lines controls the behaviour of the analytical solution, for example,
the crossover tie line is inferred to control the development of the miscibility in the combined vapourizing–condensing process. Each key tie line’s length is calculated in order to finalize the MMP. A balanced binary-tree data structure of the MMC algorithm with an increasing number of contacts is shown in Figure A1.2. A minimization function is used to calculate the MMPs until \( N \) contacts. More detailed information about these two methods can be found in the literature (Ahmadi and Johns, 2011; Orr Jr et al., 1993) and their results for the Pembina and Bakken oil cases are summarized and listed in Table A1.1. It is easily seen that the calculated MMPs from these two methods have large ADs in comparison with the measured MMPs. Moreover, neither the KTL method nor the MMC algorithm can solely calculate the MMPs in nanopores.

Another two EOS-based methods, EOS+MMC and EOS+VIT methods, are specifically stated in the Section 6.1 and used to calculate the MMP here. The results of the EOS+MMC method for the Bakken live oil–pure CO\(_2\) system were recorded in the literature (Teklu et al., 2014b), which are directly cited and listed in Table S1b. The other method, EOS+VIT method, was initially introduced in another study (S. Wang et al., 2016). Here, this method is used to calculate the MMPs for the Pembina and Bakken dead and live oil–pure and impure CO\(_2\) systems in bulk phase and nanopores, whose results are shown in Figures A1.3–A1.5 and summarized in Table A1.1b. It is found that the results from the EOS+VIT method have large ADs with the measured MMPs in bulk phase. Although there is no measured MMP data in nanopores, the results from the EOS-MMC and EOS-VIT methods seems not accurate in comparison with the results from other methods. Moreover, an abnormal value (i.e., 22.6 MPa) obtained at the porous radius of 4 nm for the Bakken live oil–pure CO\(_2\) system from the EOS+VIT method, which is higher.
than that at a larger pore radius and disagrees with the commonly-accepted conclusion, that is the MMP is decreased with the reduction of pore radius (Teklu et al., 2014b).

In summary, each above-mentioned existing empirical correlation, analytical method, or theoretical model has its own limitations and cannot solely estimate the MMP in an accurate way. By comparison, the new DIM is proven to be accurate and efficient for determining the MMPs in bulk phase and nanopores.
Table A1.1a

Comparison of the determined/calculated minimum miscibility pressures (MMPs) for the Pembina dead and live light oil–pure and impure CO$_2$ systems and the Bakken live light oil–pure CO$_2$ system in bulk phase and nanopores from this study (i.e., diminishing interface method), experimental methods (Zhang and Gu, 2016a), and five empirical correlations (Alston et al., 1985; Li et al., 2012; Shang et al., 2014; Yuan et al., 2004) at the reservoir temperature of $T_{res} = 53.0$ and 116.1°C.

<table>
<thead>
<tr>
<th>Oil–gas system</th>
<th>$T$ (°C)</th>
<th>Pore radius (nm)</th>
<th>MMP$_{exp}^a$ (MPa)</th>
<th>This study</th>
<th>Shang et al.</th>
<th>Valluri et al.</th>
<th>Li et al.</th>
<th>Yuan et al.</th>
<th>Alston et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pembina dead oil–pure CO$_2$</td>
<td>inf</td>
<td>12.4–12.9$^b$</td>
<td>12.4</td>
<td>11.7</td>
<td>7.41</td>
<td>14.1</td>
<td>11.5</td>
<td>8.95</td>
<td>17.4</td>
</tr>
<tr>
<td>Pembina live oil–pure CO$_2$</td>
<td>inf</td>
<td>15.2–15.4$^b$</td>
<td>15.0</td>
<td>20.8</td>
<td>36.03</td>
<td>14.1</td>
<td>7.80</td>
<td>13.0</td>
<td>15.26</td>
</tr>
<tr>
<td>Pembina dead oil–impure CO$_2$</td>
<td>inf</td>
<td>21.8</td>
<td>22.1</td>
<td>1.38</td>
<td>14.4</td>
<td>34.14</td>
<td>14.1</td>
<td>35.29</td>
<td>11.5</td>
</tr>
<tr>
<td>Pembina live oil–pure CO$_2$</td>
<td>100</td>
<td>–</td>
<td>15.4</td>
<td>–</td>
<td>20.8</td>
<td>–</td>
<td>14.1</td>
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<td>20.8</td>
<td>–</td>
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<td>–</td>
<td>13.0</td>
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<tr>
<td>Bakken live oil–pure CO$_2$</td>
<td>inf</td>
<td>21.4</td>
<td>24.1</td>
<td>–</td>
<td>25.3</td>
<td>–</td>
<td>24.2</td>
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<td>–</td>
<td>21.4</td>
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<td>–</td>
<td>24.2</td>
<td>–</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Notes:

- **a:** Experimentally measured MMPs
- **b:** Average value is used to calculate AD%
Table A1.1b

Comparison of the determined/calculated minimum miscibility pressures (MMPs) for the Pembina dead and live light oil–pure and impure CO₂ systems and the Bakken live light oil–pure CO₂ system in bulk phase and nanopores from this study (i.e., diminishing interface method), experimental methods (Zhang and Gu, 2016a), and some other existing theoretical methods (Alston et al., 1985; Li et al., 2012; Shang et al., 2014; Yuan et al., 2004) at the reservoir temperature of \(T_{res} = 53.0\) and 116.1°C.

<table>
<thead>
<tr>
<th>Oil–gas system</th>
<th>(T) (°C)</th>
<th>Pore radius (nm)</th>
<th>MMP(_{esp}) (^a) (MPa)</th>
<th>This study</th>
<th>KTL</th>
<th>MMC</th>
<th>EOS + MMC</th>
<th>EOS + VIT</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>MPa</td>
<td>AD%</td>
<td>MPa</td>
<td>AD%</td>
<td>MPa</td>
</tr>
<tr>
<td>Pembina dead oil–pure CO₂</td>
<td>53.0</td>
<td>inf</td>
<td>12.4–12.9(^b)</td>
<td>12.4</td>
<td>1.98</td>
<td>5.0</td>
<td>60.47</td>
<td>10.6</td>
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<tr>
<td>Pembina live oil–pure CO₂</td>
<td></td>
<td>inf</td>
<td>15.2–15.4(^b)</td>
<td>15.0</td>
<td>1.96</td>
<td>16.3</td>
<td>6.21</td>
<td>10.9</td>
</tr>
<tr>
<td>Pembina dead oil–impure CO₂</td>
<td></td>
<td>inf</td>
<td>21.8</td>
<td>22.1</td>
<td>1.38</td>
<td>27.5</td>
<td>26.15</td>
<td>25.8</td>
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<td>16.3</td>
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<td>–</td>
<td>16.3</td>
<td>–</td>
<td>10.9</td>
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<tr>
<td>Bakken live oil–pure CO₂</td>
<td>116.1</td>
<td>inf</td>
<td>–</td>
<td>24.7</td>
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<td>27.8</td>
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<td>20.6</td>
<td>–</td>
<td>27.8</td>
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<td>24.7</td>
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</tbody>
</table>

Notes:  
\(^a\): Experimentally measured MMPs  
\(^b\): Average value is used to calculate AD%
Figure A1.1 Flowchart of the semi-analytical method (key tie line method) for calculating the minimum miscibility pressures (Orr Jr et al., 1993).
Figure A1.2 Schematic diagram of the multiple-mixing cell method for calculating the minimum miscibility pressures (Ahmadi and Johns, 2011).
**Figure A1.3** Determined minimum miscibility pressures of 11.5, 12.5, and 14.2 MPa for the Pembina dead light oil–pure CO$_2$ system, Pembina live light oil–pure CO$_2$ system, and Pembina dead light oil–impure CO$_2$ system by means of the vanishing interfacial tension (VIT) technique on a basis of the calculated interfacial tensions from the modified Peng–Robinson equation of state at $T_{res} = 53.0^\circ$C, respectively.
Figure A1.4 Determined minimum miscibility pressures of 12.1, 11.5, and 11.4 MPa for the Pembina live light oil–pure CO$_2$ system by means of the vanishing interfacial tension (VIT) technique on a basis of the calculated interfacial tensions from the modified Peng–Robinson equation of state at the pore radius of 100, 20, and 4 nm and $T_{\text{res}} = 53.0^\circ$C, respectively.
Figure A1.5 Determined minimum miscibility pressures of 19.5, 18.9, and 22.6 MPa for the Bakken live light oil–pure CO₂ system by means of the vanishing interfacial tension (VIT) technique on a basis of the calculated interfacial tensions from the modified Peng–Robinson equation of state at the pore radius of 100, 20, and 4 nm and $T_{res} = 116.1^\circ\text{C}$, respectively.
APPENDIX II

In the literature, almost all existing empirical correlations for predicting the MMPs are generally expressed in mathematical equations and graphical formats. In general, the reservoir temperature, oil composition, and injection gas composition are considered as three important factors affecting the MMP. Thus the existing correlations are reviewed and categorized as a function of the three important factors in Tables A2.1–A2.3: Type I–temperature dependent, Type II–temperature and oil composition dependent, and Type III–temperature, oil composition, and gas composition dependent. A detailed summary of 40 commonly-used existing correlations for predicting the MMPs are analyzed and listed as follows.
### Table A2.1 Summary of the existing correlations: Type I–temperature dependent.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Correlation/Model</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1976</td>
<td>National Petroleum Council</td>
<td>(MMP = 12.6472 + 0.015531 - (1.8T_R + 32) + 1.24192 \times 10^{-4} \times (1.8T_R + 32)^2 - \frac{716.9427}{(1.8T_R + 32)})</td>
<td>• 35.0°C &lt; (T_R) &lt; 88.9°C&lt;br&gt;• (P_b) is considered to be the MMP if (MMP &lt; P_b)</td>
</tr>
<tr>
<td>1979</td>
<td>Lee</td>
<td>(MMP = 7.3924 \times 10^b, b = 2.772 - \left(\frac{1519}{492 + 1.8T_R}\right))</td>
<td></td>
</tr>
<tr>
<td>1980</td>
<td>Yellig and Metcalfe</td>
<td>(MMP = 12.6472 + 0.015531 - (1.8T_R + 32) + 1.24192 \times 10^{-4} \times (1.8T_R + 32)^2 - \frac{716.9427}{(1.8T_R + 32)})</td>
<td>• 35.0°C &lt; (T_R) &lt; 88.9°C&lt;br&gt;• (P_b) is considered to be the MMP if (MMP &lt; P_b)</td>
</tr>
<tr>
<td>1984</td>
<td>Orr and Jensen</td>
<td>(MMP = 0.101386 \times e^{\left[10.91 - \left(\frac{2015}{255.373 + 0.5556(1.8T_R + 32)}\right)\right]})</td>
<td>• (T_R &lt; 49.0°C)</td>
</tr>
<tr>
<td>1985</td>
<td>Sebastian et al.</td>
<td>(F_{\text{impure}} = 1.0 - 2.13 \times 10^{-2}(T_{\text{cm}} - 304.2) + 2.51 \times 10^{-4}(T_{\text{cm}} - 304.2)^2 - 2.35 \times 10^{-7}(T_{\text{cm}} - 304.2)^3,) where (T_{\text{cm}} = \sum x_i \times T_{ci})</td>
<td>• (H_2S) critical temperature is modified to 51.67°C</td>
</tr>
<tr>
<td>2015</td>
<td>Dong and Liu</td>
<td>(MMP = -4.8913 + 0.0415T_R - 0.0015974 T_R^2)</td>
<td>–</td>
</tr>
</tbody>
</table>
Table A2.2 Summary of the existing correlations: Type II—temperature and oil composition dependent.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Correlation/Model</th>
<th>Notes</th>
</tr>
</thead>
</table>
| 1974 | Holm and Josendal | A graphical correlation that is a function of reservoir temperature and molecular weight of C₅⁺ of the crude oil | - 180 < MW_C5⁺ < 240  
- 32.2°C < TR < 82.2°C  
- 9.65 MPa < P < 22.0 MPa |
| 1978 | Cronquist     | $MMP = 0.11027 \times (1.8T_R + 32)^{(0.744206 \times 0.0011038 + 0.0015279)}$           | - 21.7°C < TR < 120.8°C  
- 23.7 < °API < 44.8  
- 7.4 MPa < MMP< 34.5 MPa |
| 1981 | Mungan        | A graphical correlation that is a function of reservoir temperature and molecular weight of C₅⁺ of the crude oil (extended Holm–Josendal correlation) | - 180 < MW_C5⁺ < 340  
- 32.2°C < TR < 82.2°C  
- 9.65 MPa < P < 22.0 MPa |
| 1983 | Orr and Taber | 1. Determine the CO₂ density at the MMP at some temperature from a correlation or by slim-tube tests;  
2. Use an EOS to calculate the pressure required to produce the same density when contaminants are added to the CO₂ or the temperature is changed, this pressure is the estimated MMP. | - |
| 1985 | Glaso et al.  | For $x_{INT} > 18$ mol. %: $MMP = 5.5848 - 2.3470 \times 10^{-2} MW_{C7+} + 1.1721 \times 10^{-11} MW_{C7+}^{3.73} e^{7868 MW_{C7+}^{1.08}} (1.8T_R + 32)$  
For $x_{INT} < 18$ mol. %: $MMP = 20.3251 - 2.3470 \times 10^{-2} MW_{C7+} + 1.1721 \times 10^{-11} MW_{C7+}^{3.73} e^{7868 MW_{C7+}^{1.08}} (1.8T_R + 32) - 8.3564 \times 10^{-1} x_{INT}$ | Effect of the intermediates (C₂-C₆) components is considered only when $x_{INT} < 18\%$ |
<p>| 1985 | Alston        | $MMP = 6.0536 \times 10^{-6} (1.8T_R + 32)^{1.06} (MW_{C5+})^{1.78} (\frac{X_{VOL}}{X_{INT}})^{0.136}$ | $P_b$ is considered to be the MMP if $MMP &lt; P_b$ |</p>
<table>
<thead>
<tr>
<th>Year</th>
<th>Authors</th>
<th>Equation</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>Firoozabadi and Aziz</td>
<td>( \text{MMP} = 6.0536 \times 10^{-6} (1.8T_R + 32)^{1.06}(MW_{C5+})^{1.78} )</td>
<td>When ( \text{Pb} &lt; 0.345 \text{ MPa} ), ( \text{MMP} = 6.0536 \times 10^{-6} (1.8T_R + 32)^{1.06}(MW_{C5+})^{1.78} ) ( \text{Impurity correction factor} ) [ F_{\text{impure}} = \left( \frac{87.8}{1.8T_{\text{cm}} + 32} \right)^{2.84}, \text{ where } T_{\text{cm}} = \sum w_i + T_{\text{ci}} )</td>
</tr>
<tr>
<td>1988</td>
<td>Enick et al.</td>
<td>( \text{MMP} = 9433 - 188 \times 10^3(\frac{x_{\text{INT}}}{MW_{C7+}T^{0.25}}) + 1.4 \times 10^6(\frac{x_{\text{INT}}}{MW_{C7+}T^{0.25}})^2 )</td>
<td>A graphical correlation that is a function of the reservoir temperature and molecular weight of ( \text{C}_{5+} ) of the crude oil</td>
</tr>
<tr>
<td>1993</td>
<td>Zou et al.</td>
<td>( \text{MMP} = 44.3 - 169.5(\frac{x_{\text{INT}}}{MW_{C7+}T^{0.25}}) + 513.11(\frac{x_{\text{INT}}}{MW_{C7+}T^{0.25}})^2 )</td>
<td>On a basis of the artificial neural network model, the pure CO(<em>2) MMP is correlated with the reservoir temperature, molecular weight of ( \text{C}</em>{5+} ), and concentration of volatiles (CH(_4)) and intermediates (C(_2)-4) in the oil</td>
</tr>
<tr>
<td>2003</td>
<td>Huang et al.</td>
<td>( \text{MMP} = 5.0093 \times 10^{-5}(1.8T_R + 32)^{1.164}(MW_{C5+})^{1.2785}(\frac{x_{\text{VOL}}}{x_{\text{INT}}})^{0.1073} )</td>
<td>On a basis of the artificial neural network model, the pure CO(<em>2) MMP is correlated with the reservoir temperature, molecular weight of ( \text{C}</em>{5+} ), and concentration of volatiles (CH(_4)) and intermediates (C(_2)-4) in the oil</td>
</tr>
<tr>
<td>2005</td>
<td>Emera–Sarma</td>
<td>For ( \text{Pb} &gt; 0.345 \text{ MPa} : ) ( \text{MMP} = 5.0093 \times 10^{-5}(1.8T_R + 32)^{1.164}(MW_{C5+})^{1.2785}(\frac{x_{\text{VOL}}}{x_{\text{INT}}})^{0.1073} )</td>
<td>For ( \text{Pb} &gt; 0.345 \text{ MPa} : ) ( \text{MMP} = 5.0093 \times 10^{-5}(1.8T_R + 32)^{1.164}(MW_{C5+})^{1.2785} )</td>
</tr>
<tr>
<td>2005</td>
<td>Yuan et al.</td>
<td>( \text{MMP}<em>{\text{pure}} = a_1 + a_2MW</em>{C7+} + a_3x_{C,2-4} + (a_4 + a_5MW_{C7+} + a_6x_{C,2-6})T_R + (a_7 + a_8MW_{C7+} + a_9MW_{C7+} + a_{10}x_{C,2-6})T_R^2 )</td>
<td>( \text{MMP}<em>{\text{pure}} = a_1 + a_2MW</em>{C7+} + a_3x_{C,2-4} + (a_4 + a_5MW_{C7+} + a_6x_{C,2-6})T_R + (a_7 + a_8MW_{C7+} + a_9MW_{C7+} + a_{10}x_{C,2-6})T_R^2 )</td>
</tr>
</tbody>
</table>

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Table showing correlations for different conditions and authors.
<table>
<thead>
<tr>
<th>Year</th>
<th>Author(s)</th>
<th>MMP Equation</th>
<th>Conditions</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>Shokir et al.</td>
<td>(MMP = -0.068616z^3 + 0.31733z^2 + 4.9804z + 13.432), where (z = \sum_{i=1}^{4} z_i, z_i = A_3 y_i^3 + A_2 y_i^2 + A_1 y_i + A_0)</td>
<td>(185 &lt; MW_{C5+} &lt; 268)</td>
<td></td>
</tr>
<tr>
<td>2012</td>
<td>Li et al.</td>
<td>(MMP = 7.30991 \times 10^{-5} \left[ \ln(1.8T_R + 32) \right]^{5.33647} \left[ \ln(MW_{C7+}) \right]^{2.08836} \left( 1 + \frac{x_{\text{VOL}}}{x_{\text{INT}}} \right) \frac{2.01658 \times 10^{-1}}{x_{\text{INT}}})</td>
<td>(32.2^\circ C &lt; T_R &lt; 112.2^\circ C)</td>
<td>Only applicable for pure CO2</td>
</tr>
<tr>
<td>2012</td>
<td>Khanzode et al.</td>
<td>(MMP = a_1 + a_2 x_{\text{C2-6}} + a_3 x_{\text{C7+}} + a_4 MW_{C7+} + [a_5 + a_6 x_{\text{C2-6}} + a_7 x_{\text{C7+}} + a_8 MW_{C7+} + a_9 T_R + a_{10} (1 + \frac{x_{\text{VOL}}}{x_{\text{INT}}})] T_R + a_{11} (1 + \frac{x_{\text{VOL}}}{x_{\text{INT}}}) T_R)</td>
<td>(6.9 \text{ MPa} &lt; P &lt; 28.2 \text{ MPa})</td>
<td>–</td>
</tr>
<tr>
<td>2012</td>
<td>Ju et al.</td>
<td>(MMP = -0.04562 S^3 + 0.33399 S^2 + 4.9811 S + 13.569) where (S = \sum_{i=1}^{8} S_i, S_i = a_i + b_i x_i + c_i x_i^2 + d_i x_i^3)</td>
<td>(P &lt; 40.0 \text{ MPa})</td>
<td>–</td>
</tr>
<tr>
<td>2013</td>
<td>Chen et al.</td>
<td>(MMP = 3.9673 \times 10^{-2} T_R^{0.8293} (MW_{C7+})^{0.5382} (x_{\text{C1+N2}})^{0.1018} (x_{\text{C2-6}})^{-0.2316})</td>
<td>(185 &lt; MW_{C7+} &lt; 249)</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>Kaydani et al.</td>
<td>(MMP = 0.2683 T_R + 0.2683 MW_{C5+} + 0.2683 T_R (T_R - x_{\text{INT}})^2 + 0.3339 T_R (T_R + x_{\text{VOL}} - x_{\text{INT}}) + 0.1161)</td>
<td>(32.2^\circ C &lt; T_R &lt; 118.3^\circ C)</td>
<td>–</td>
</tr>
<tr>
<td>2014</td>
<td>Shang et al.</td>
<td>For pure CO2, (MMP = \exp{ (T_R^b + g) [\ln(MW_{C7+})]^c + h(\exp(\frac{x_{\text{VOL}}}{x_{\text{INT}}})]^d + j)(x_{C7+})^f }) For (x_{\text{CO2}} &lt; 0.5) (mole fraction) (MMP = \exp{ a T_R^b E_x^c f^{x_{\text{CO2}}} + D^m i^{x_{\text{S}}} (x_{C7+})^d - g^{x_{\text{S}}} h^{x_{\text{C2+C}}} }) For (x_{\text{CO2}} &gt; 0.5) (mole fraction) (MMP = (a T_R^b + E^c D^f (\exp(x_{\text{CO2}}))^g) (x_{C7+})^d (h^{x_{\text{S}}} i^{x_{\text{C2+C}}} + j) + T_R^m)</td>
<td>Not applicable for live oil case and impure gas with some intermediate components</td>
<td>–</td>
</tr>
<tr>
<td>Year</td>
<td>Authors</td>
<td>Equation</td>
<td>MMP Conditions (°C/MPa)</td>
<td></td>
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<tr>
<td>------</td>
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<td>----------------------------------------------------------------------------</td>
<td>------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>Dong and Liu</td>
<td>$E = (MW_{C7+})^{3\text{exp}/3\text{int}}, D = \exp(x_{N_2}) \exp(x_{CH_4}) / \exp(x_{CO_2})$</td>
<td>$130 &lt; MW_{C7+} &lt; 402.7$</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>Zhang et al.</td>
<td>$MMP = 675.01 - 6.93MW_{C6+} + 1.7(T_R - T_{ci})$</td>
<td>$21.7°C &lt; T_R &lt; 192.0°C$</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>Zhang et al.</td>
<td>$MMP = 8.3397 \times 10^{-5}[\ln(1.8T_R + 32)]^{3.9774}[\ln(MW_{C7+})]^{3.3179}(1 + \frac{x_{\text{VOL}}}{x_{\text{INT}}})^{0.17461}$</td>
<td>$0 \text{ MPa} &lt; P &lt; 70.0 \text{ MPa}$</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>ZareNezhad</td>
<td>$MMP = 43.568 - 16.239(\frac{x_{C2-6}}{MW_{C7+} T^{0.25}}) + 333.615(\frac{x_{C2-6}}{MW_{C7+} T^{0.25}})^2 - 0.146x_{C2+}^{1.455}MW_{C2+}^{0.19}$</td>
<td>$120 &lt; MW_{C7+} &lt; 302$</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>Lai et al.</td>
<td>$MMP = 0.1447R + \ln x_{CO_2} - 0.051x_{N_2} - 0.533x_{C_1} - 0.782x_{C_i} - 1.471x_{C_i} + 0.029x_{C_2} + 0.055x_{C_i} - 0.723x_{C_i} - 3.429x_{C_i} + 0.265x_{C_i}^2 - 0.554x_{C_i}$</td>
<td>$53.9°C &lt; T_R &lt; 148.9°C$</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>Valluri et al.</td>
<td>$MMP = 0.3123T_R^{0.985}MW_{C_{5+}}^{0.7421}$</td>
<td>Limited to the dead oil–pure CO$_2$ system</td>
<td></td>
</tr>
</tbody>
</table>
Table A2.3 Summary of the existing correlations: Type III–temperature, oil composition, and gas composition dependent.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Correlation/Model</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981</td>
<td>Johnson and</td>
<td>$\text{MMP} - P_{\text{C,inj}} = \alpha_{\text{inj}}(T_R - T_{\text{C,inj}}) + I(\beta M - M_{\text{inj}})^2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pollin</td>
<td>where, $I = -11.73 + 6.313 \times 10^{-2} \times M - 1.954 \times 10^{-4} \times M^2 + 2.502 \times 10^{-7} \times M^3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta = 0.285$</td>
<td>• 26.9°C &lt; $T_R$ &lt; 136.9°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for pure CO$<em>2$, $\alpha</em>{\text{inj}} = 0.13\text{MPa}/^\circ K$;</td>
<td>• Less than 10 mol.% impurities in injection gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for N$<em>2$ impurity $\alpha</em>{\text{inj}} = 0.0722(1.8 + \frac{10^3 y}{T_R - T_{\text{C,inj}}})$;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>for C$<em>1$ impurity $\alpha</em>{\text{inj}} = 0.0722(1.8 + \frac{10^5 y}{T_R - T_{\text{C,inj}}})$;</td>
<td></td>
</tr>
<tr>
<td>1985</td>
<td>Kovarik</td>
<td>$\text{MMP}<em>{\text{impure}} = 40.8(548 - T</em>{pc}) + P_{\text{pure}}$, where $T_{cm} = \sum y_i T_{ci}$</td>
<td>-</td>
</tr>
<tr>
<td>1986</td>
<td>Harmon and</td>
<td>MMP is the pressure at which a marked increase in vapour-phase density occurs.</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Grigg</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>Orr and Silva</td>
<td>$\rho_{\text{MMP}} = -0.524 \times F + 1.189$, when $F &lt; 1.467$;</td>
<td>• MMP is obtained at $T_R$ and $\rho_{\text{MMP}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\rho_{\text{MMP}} = 0.42$, when $F &gt; 1.467$, where $F = \sum_{i=2}^{37} K_i \times w_{i\text{C}_2}$, and log($K_i$) $= 0.7611 - 0.04175 \times C_i$</td>
<td>• Used for pure and contaminated CO$_2$ injection</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Cannot predict the presence of C$_1$ and other non-hydrocarbons in oil</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• $P_b$ is considered to be the MMP if MMP $&lt; P_b$</td>
</tr>
<tr>
<td>Year</td>
<td>Author(s)</td>
<td>MMP Equation</td>
<td>Notes</td>
</tr>
<tr>
<td>------</td>
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</tr>
<tr>
<td>1988</td>
<td>Eakin and Mitch</td>
<td>[ \ln P_r = \ln \left( \frac{MMP}{P_r} \right) = \left( 0.1697 - \frac{0.06912}{T_r} \right) y_{C1} (MW_{C7-})^{0.5} + (2.3865 - 0.005955 \frac{MW_{C7-}}{T_r}) y_{C2+} ] + \left( 0.1776 - \frac{0.01023}{T_r} \right) y_{N2} (MW_{C7-})^{0.5} + [0.01221 MW_{C7-} - 0.0005899 \left( \frac{MW_{C7-}}{T_r} \right)^3] y_{CO2} ] + \left[ 101.429 \frac{MW_{C7-}}{T_r} + 0.003750 \right] y_{H2S}</td>
<td>–</td>
</tr>
<tr>
<td>1993</td>
<td>Zou et al.</td>
<td>[ MMP^* = 44.3 - 169.5 \left( \frac{x_{\text{INT}}}{MW_{C7-} T^{0.25}} \right) + 513.11 \left( \frac{x_{\text{INT}}}{MW_{C7-} T^{0.25}} \right)^2 ] For ( y_{CH4} &lt; 80 \text{ mol.%} ), ( MMP = MMP^* \times \frac{y_{CH4}^{1.4456}}{y_{\text{INT}}^{0.0853}} )</td>
<td>Only applicable for pure CO₂ and enable to differentiate the MMPs for dead and live oil samples</td>
</tr>
<tr>
<td>2005</td>
<td>Yuan et al.</td>
<td>[ MMP_{\text{pure}} = a_1 + a_2 MW_{C7-} + a_3 x_{C2-6} + (a_4 + a_5 MW_{C7-} + a_6 \frac{x_{C2-6}}{MW_{C7-}}) T_R + (a_7 + a_8 MW_{C7-} + a_9 MW_{C7-} + a_{10} x_{C2-6}) T_R^2 ] [ \frac{MMP_{\text{imp}}}{MMP_{\text{pure}}} = 1 + m(\gamma_{CO2} - 100) ] [ m = a_1 + a_2 MW_{C7-} + a_3 x_{C2-6} + (a_4 + a_5 MW_{C7-} + a_6 \frac{x_{C2-6}}{MW_{C7-}}) T_R + (a_7 + a_8 MW_{C7-} + a_9 MW_{C7-} + a_{10} x_{C2-6}) T_R^2 ]</td>
<td>( 139 &lt; MW_{C7-} &lt; 319 ) ( 21.7^\circ C &lt; T_R &lt; 148.0^\circ C ) ( P &lt; 70.0 \text{ MPa} )</td>
</tr>
<tr>
<td>2006</td>
<td>Shariatpanahi</td>
<td>For ( y_{CH4} &lt; 80 \text{ mol.%} ), ( MMP = \frac{MW_{C7-}^{3.534} y_{\text{INT}}^{0.7285}}{x_{C3-1}^{0.052} MW_{C2-6}^{0.052} MW_{C2-6}^{0.052}} + \frac{1}{y_{C1}^{1.0072} y_{C2-7}^{2.75} MW_{C2-4}^{2.75}} )</td>
<td>–</td>
</tr>
<tr>
<td>2010</td>
<td>Maklavanani et al.</td>
<td>[ MMP = 43.664 - 4.542 \alpha + 0.689 \alpha^2 - 0.132 \beta ] where ( \alpha = \frac{x_{C2-6}^{1.7278} x_{C1}^{0.1}}{MW_{C7-} (1.8 T_R + 32)^0.5} ), ( \beta = y_{C2+}^{1.0664 + 0.0068 MW_{C2+}} )</td>
<td>Only applicable for pure CO₂ if no ( y_{C2+} ) in injection gas</td>
</tr>
<tr>
<td>2013</td>
<td>Ghorbani</td>
<td>[ MMP = 44.162 - 4.32 \alpha + 0.691 \alpha^2 - 0.141 \beta ] where ( \alpha = \frac{x_{C2-6}^{1.68} x_{C1}^{0.1}}{MW_{C7-} (1.8 T_R + 32)^0.5} ), ( \beta = y_{C2+}^{1.085 + 0.0056 MW_{C2+}} )</td>
<td>Only applicable for pure CO₂ if no ( y_{C2+} ) in injection gas</td>
</tr>
<tr>
<td>2014</td>
<td>Liao et al.</td>
<td>[ MMP_{\text{pure}} = 0.003 \times T_R^{0.544} (MW_{C5+})^{1.006} \left( \frac{y_{\text{VOL}}}{y_{\text{INT}}} \right)^{0.143} ]</td>
<td>Enable to differentiate the MMPs for dead and live oil samples</td>
</tr>
<tr>
<td>Year</td>
<td>Author</td>
<td>MMP Equation</td>
<td>Constraints</td>
</tr>
<tr>
<td>------</td>
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<td>-------------------------------------------------------------------------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>2014</td>
<td>Alomair and Iqbal</td>
<td>$MMP = -312.040 - 7.753(A) - 2.105(B) - 9.954(C) + 5.847\left(MW_{C7+}\right) + 12.638(T_R)$</td>
<td>where A, B, C are three direct and/or indirect correlations of the non-hydrocarbons</td>
</tr>
<tr>
<td>2016</td>
<td>Khazam et al.</td>
<td>$MMP = 11664 - 2.179 \times P_b + 9.7 \times T_R - 156.2 \times 9 API - 10695651 \times \left(\frac{y_{C2-6}}{MW_{C7}, T_R}\right) + 0.00033 \times P_b^2$ $+ 5166348768 \times \left(\frac{y_{C2-6}}{MW_{C7}, T_R}\right)^2 + 2221 \times P_b \times \left(\frac{y_{C2-6}}{MW_{C7}, T_R}\right)$</td>
<td>$10.6 \text{ MPa} &lt; P &lt; 43.1 \text{ MPa}$ $28 &lt; 9 API &lt; 50$</td>
</tr>
</tbody>
</table>
APPENDIX III

The hybrid micro- and nanofluidic chip, which consists of two short micro-channels with a dimension of 3 mm (length) × 20 μm (width) × 10 μm (depth), four long micro-channels with a dimension of 20 mm (length) × 20 μm (width) × 10 μm (depth), and eleven nano-channels with a dimension of 0.5 mm (length) × 10 μm (width) × 100 nm (depth), was manufactured in double-sided and polished silicon wafers (thickness = 200 μm) with low-stress silicon nitride on both sides and shown in Figure 7.1a. The ends of all nano-channels were connected to the micro-channels. The schematic diagram demonstrating the fabrication process on the cross-sectional perspective is shown in Figure 7.1b. In brief, the patterns of the channels on the hybrid chip were first generated through AutoCAD and then transferred onto a mold. Then, a series of eleven nano-channels were defined by a deep reactive ion etch through the back side of the wafer, whose interval are kept at 300 μm. Afterwards, two micro-channels were defined and perpendicularly connected to the both sides of the nano-channels. The four inlet and/or outlet micro-channels were fabricated and connected to the two micro-channels (which were connected with the nano-channels) in a “Y” shape. Finally, the front side of the chip was anodically bonded to a thin Pyrex cover slip and the bonding process was conducted for at least half hour at T = 400 °C with a voltage of 1 kV. Each chip was rinsed with some industrial reagent fluids in order to ensure the surface conditions of the micro- and nano-channels are in the good conditions.