PHASE BEHAVIOUR AND MASS TRANSFER OF SOLVENT(S)-CO₂-HEAVY OIL SYSTEMS UNDER RESERVOIR CONDITIONS

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Huazhou Li

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Huazhou Li, candidate for the degree of Doctor of Philosophy in Petroleum Systems Engineering, has presented a thesis titled, Phase Behaviour and Mass Transfer of Solvent(s)-CO₂-Heavy Oil Systems Under Reservoir Conditions, in an oral examination held on May 14, 2013. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner: Dr. Gordon R. Moore, University of Calgary
Supervisor: Dr. Daoyong Yang, Petroleum Systems Engineering
Committee Member: *Dr. Yongan Gu, Petroleum Systems Engineering
Committee Member: Dr. Farshid Torabi, Petroleum Systems Engineering
Committee Member: Dr. Guoxiang Chi, Department of Geology
Chair of Defense: Dr. Cory Butz, Faculty of Science

*Not present at defense, submitted questions
ABSTRACT

CO₂ has been found to be an efficient agent for recovering heavy oil resources worldwide through an immiscible displacement process. One major disadvantage of CO₂ immiscible process is the limited solubility of CO₂ in heavy oil, resulting in limited enhanced oil recovery. Addition of light alkane solvents to CO₂ stream may provide a better recovery efficiency of heavy oil, though it is not well understood how addition of solvents will affect the phase behaviour and mass transfer of CO₂-heavy oil systems. Therefore, it is of fundamental and practical importance to study phase behaviour and mass transfer of the solvent(s)-CO₂-heavy oil systems under reservoir conditions.

In order to improve the phase behaviour modeling of highly asymmetric systems, e.g., solvent(s)-CO₂-heavy oil systems, a new alpha function for the Peng-Robinson equation of state (PR EOS) is first developed. In comparison with the existing alpha functions evaluated in this study, the modified alpha function with the redefined acentric factor at a reduced temperature of 0.6 provides more accurate prediction of vapour pressures of non-hydrocarbon and hydrocarbon compounds, especially heavy hydrocarbons. Subsequently, the enhanced swelling effect and viscosity reduction of CO₂-heavy oil systems with the addition of solvent C₃H₈ or n-C₄H₁₀ are experimentally measured and theoretically determined. An increased swelling effect of heavy oil is obtained by adding gas solvent C₃H₈ or n-C₄H₁₀ into the CO₂ stream, while an enhanced viscosity reduction of the CO₂-heavy oil system is also achieved in the presence of either solvent C₃H₈ or n-C₄H₁₀. By treating the heavy oil sample as a single pseudocomponent, three binary interaction parameter (BIP) correlations have been proposed for respectively characterizing CO₂-heavy oil binaries, C₃H₈-heavy oil binaries and n-C₄H₁₀-heavy oil binaries. The PR EOS
with the modified alpha function and BIP correlations can be used to predict the saturation pressures and swelling factors of the aforementioned systems with a generally good accuracy.

Equilibrium interfacial tensions (IFT) between solvent(s)-CO₂ mixture and heavy oil have also been experimentally measured with an axisymmetric drop shape analysis (ADSA) setup. Addition of C₃H₈ and/or n-C₄H₁₀ into CO₂ stream leads to an obvious reduction of IFT between heavy oil and CO₂, though the degree of reduction depends on the added amount of the light alkane solvent(s). Theoretically, an optimized mechanistic parachor model provides a qualitative agreement with the measured equilibrium IFTs between solvent(s)-CO₂ mixture and heavy oil.

The liquid-liquid-vapour (L₁L₂V) phase boundaries of solvent(s)-CO₂ heavy oil mixtures in the pressure-temperature (P-T) diagram are also experimentally and visually determined with the PVT setup. The addition of an alkane solvent to the CO₂-heavy oil system tends to expand the pressure span of the L₁L₂V phase boundary, while the L₁L₂V phase boundary of solvent(s)-CO₂-heavy oil system shows its tendency to move towards the high-temperature and low-pressure side of the P-T diagram.

Experimental and theoretical methods have been performed to determine the diffusion coefficient of each component in the solvent(s)-CO₂ mixture or the apparent diffusion coefficient of the mixture in heavy oil. It is found that the gas-phase solvent fraction decreases as diffusion proceeds, while the gas-phase CO₂ fraction decreases during the diffusion test. As for the solvent(s)-CO₂ mixtures tested, the molecular diffusion coefficient of an individual solvent in heavy oil is found to be significantly larger than that of CO₂ in heavy oil. Also, at the same pressure, the C₃H₈-CO₂ mixture leads to an accelerated growth in swelling-factor compared to pure CO₂.
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NOMENCLATURE

\( a \) attraction parameter in Equations [3-1]

\( a_c \) constant in Equation [3-2]

\( a_1, a_2, \ldots, a_{12} \) empirical constants

\( A \) cross-sectional area of the diffusion cell, cm\(^2\)

% AAD percentage average absolute deviation

ADSA axisymmetric drop shape analysis

\( b \) van der Waals volume, m\(^3\)/kmol

\( b_1, b_2, \ldots, b_7 \) empirical constants

\( B \) constant in Equation [3-28]

% BIAS percentage bias

BIP binary interaction parameter

\( c_i \) concentration of \( i \)th component in heavy oil in mole fraction

\( c_{i,\text{sat}} \) saturation concentration of \( i \)th component in heavy oil in mole fraction

\( c_1, c_2, \ldots, c_7 \) empirical constants in Equations [2-4] and [2-5]

\( C \) volume correction factor, m\(^3\)/kmol

\( C_n \) carbon number

\( d, e, f, g, h, l, n \) coefficients in Equations [4-3] and [4-6]

\( d_1, d_2, d_3 \) empirical constants in Equation [2-6]

\( D_{AB} \) diffusivity of solute A in solvent B, m\(^2\)/s

xx
$D_i$ \hspace{1cm} \text{individual molecular diffusion coefficient of the } i\text{th component in heavy oil, m}^2/\text{s}

$F, G, H, K$ \hspace{1cm} \text{coefficients in Equation [4-16]}

$H$ \hspace{1cm} \text{enthalpy, kJ/mol}

$H_{CO_2}$ \hspace{1cm} \text{Henry's constant}

$H^{IG}$ \hspace{1cm} \text{ideal gas enthalpy, kJ/mol}

$\Delta_i^g H(T)$ \hspace{1cm} \text{enthalpy of vaporization at temperature } T, \text{ kJ/mol}

$i$ \hspace{1cm} \text{integer}

IFT \hspace{1cm} \text{interfacial tension}

$k$ \hspace{1cm} \text{characteristic constant in Equations [3-9] and [3-10], temperature-dependant characteristic factor in Equation [4-2]}

$k_1$ \hspace{1cm} \text{characteristic constant in Equations [3-11] and [3-13], coefficient in Equation [7-10]}

$k'_1$ \hspace{1cm} \text{characteristic constant in Equation [3-12]}

$k_2$ \hspace{1cm} \text{characteristic constant in Equations [3-11]-[3-13], coefficient in Equation [7-10]}

$l$ \hspace{1cm} \text{constant in Equation [3-13]}

$L_0$ \hspace{1cm} \text{initial height of heavy oil in diffusion cell, m}

$L(t)$ \hspace{1cm} \text{height of gas-diluted heavy oil in diffusion cell at a given time, m}

$L_1, L_2, L_m$ \hspace{1cm} \text{liquidity of solvent, solute and mixture, respectively}

$m$ \hspace{1cm} \text{total number of compound species}
$m_1, m_2$ coefficients in Equation [7-10]

$M$ molar mass, g/mol

% MAD percentage maximum absolute deviation

$MW$ molecular weight

$n$ number of coexisting phases in Equation [2-1]

$n_j$ molar mass of $j$th component in liquid bulk phase, mol

$nc$ number of components in the system

$ng$ number of gas-phase components in the system

$N$ total number of data point

$NPTS$ number of data points

$O(c)$ objective function

$P$ pressure, kPa

$Pa$ Parachor

$P_{ao}$ Parachor of Lloydminster heavy oil

$P_c$ critical pressure, kPa

$P_{eq}$ equilibrium pressure, kPa

$P_r$ reduced pressure

$P_{v}^{cal}$ calculated vapour pressure, kPa

$P_{v}^{exp}$ experimental vapour pressure, kPa

$\Delta P$ differential pressure, kPa

PR EOS Peng-Robinson equation of state
\( Q \)  
flow rate, \( \text{cm}^3/\text{min} \)

\( R \)  
universal gas constant, \( J/(\text{mol} \cdot \text{K}) \)

\( R_g \)  
gas solubility in oil

\( RMSRE \)  
root-mean-squared relative error

\( SF \)  
swelling factor

\( SG \)  
specific gravity

\( t \)  
time, s

\( T \)  
temperature, K

\( T_{br} \)  
reduced temperature at normal boiling point, K

\( T_c \)  
critical temperature, K

\( T_r \)  
reduced temperature

\( V \)  
molar volume, \( \text{m}^3/\text{kmol} \)

\( V_A \)  
molar volume at normal boiling point, \( \text{m}^3/\text{kmol} \)

\( V_c \)  
critical molar volume, \( \text{m}^3/\text{kmol} \)

\( V_{\text{corrected}} \)  
corrected molar volume, \( \text{m}^3/\text{kmol} \)

\( V_{s1} \)  
molar volume of oil at saturation temperature and atmospheric pressure, \( \text{m}^3/\text{kmol} \)

\( V_{s2} \)  
molar volume of saturated oil at saturation temperature and pressure, \( \text{m}^3/\text{kmol} \)

\( V(t) \)  
molar volume of solvent-diluted oil at time \( t \), \( \text{m}^3/\text{kmol} \)
\( V_0 \)  molar volume of heavy oil at the beginning of pressure decay experiment, \( m^3/kmol \)

\( V^* \)  molar volume of heavy oil at 60°F

\( w \)  weight fraction

\( x_i \)  mole fraction of the \( i \)th component in the bulk liquid phase, distance from the bottom of the diffusion cell in \( x \)-direction, \( m \)

\( x_i^{\text{cal}} \)  calculated mole fraction of \( i \)th component in heavy oil

\( x_i^{\text{exp}} \)  measured mole fraction of \( i \)th component in heavy oil

\( X \)  solvent solubility in mole fraction

\( X_i^{\text{cal}} \)  calculated solvent solubility of \( i \)th data point in heavy oil

\( X_i^{\text{exp}} \)  measured solvent solubility of \( i \)th data point in heavy oil

\( y \)  parameter in Equation [2-4]

\( y_i \)  mole fraction of the \( i \)th component in the vapour phase

\( Z \)  compressibility factor

\( Z_i \)  compressibility factor of liquid phase

\( Z_{RA} \)  Rackett parameter

\( Z_v \)  compressibility factor of vapour phase

**Greek letters**

\( \alpha \)  empirical constant having a value in the range of 0 to 1 in Equation [2-12b]; and alpha function in Equation [3-2]

\( \beta \)  parameter in Equation [4-5b]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )</td>
<td>IFT, mN/m</td>
</tr>
<tr>
<td>( \delta_{ij} )</td>
<td>BIP between ( i )th component and ( j )th component</td>
</tr>
<tr>
<td>( \mu )</td>
<td>viscosity, mPa\cdot s</td>
</tr>
<tr>
<td>( \rho )</td>
<td>density, kg/cm(^3)</td>
</tr>
<tr>
<td>( \rho^L, \rho^V )</td>
<td>molar densities of liquid and vapour phases, mol/cm(^3)</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>surface tension, mN/m</td>
</tr>
<tr>
<td>( \phi )</td>
<td>volume fraction</td>
</tr>
<tr>
<td>( \omega )</td>
<td>acentric factor defined at ( T_r = 0.7 )</td>
</tr>
<tr>
<td>( \omega' )</td>
<td>acentric factor defined at ( T_r = 0.6 )</td>
</tr>
</tbody>
</table>
CHAPTER 1 INTRODUCTION

1.1 CO₂-based Processes for Heavy Oil Recovery

Heavy oil and tar sands are an important part of the energy supply of the world, while they have been exploited increasingly as the demand for petroleum increases (Farouq Ali, 2003). Canada’s energy future depends on heavy oil resources that are mainly discovered in Saskatchewan and Alberta, of which only 8-9% of the original oil in place (OOIP) can be recovered with currently available technologies due to the fact that the oil is highly viscous and contained in thin payzones.

About 62% of Canada’s total heavy oil resources is discovered in Saskatchewan (Bowers and Drummond, 1997), including 3.4 billion m³ of proved reserves in the west-central region of the province (Ministry of Energy and Resources of Saskatchewan, 2008). As for the proved heavy oil reserves in Saskatchewan, about 97% is contained in payzones of less than 10 m, while 55% is located in payzones of less than 5 m (Strivastava et al., 1999). The depth of these thin payzones ranges from 300 m to 1400 m, while a large portion of these reservoirs are underlain by a bottomwater. These heavy oils possess high carbon intensity, require more effort and energy to recover than the conventional oils, resulting in adverse environmental consequences during exploitation. The major challenge lies in developing techniques for recovering these heavy oil resources while minimizing greenhouse gas emissions (mainly CO₂) and thus reducing the carbon footprint.
It has been found that cyclic steam stimulation (CSS), steam-assisted gravity drainage (SAGD) and vapour extraction (VAPEX) often do not work for recovering heavy oil in such thin reservoirs (Dyer and Farouq Ali, 1994). Alternatively, CO₂ has been found to be an efficient agent for recovering heavy oil resources worldwide through an immiscible displacement process (Saner and Patton, 1986; Mohammed-Singh and Singhal, 2005; Sahin et al., 2008). Such immiscible displacement processes mainly include CO₂ cyclic injection (i.e., CO₂ huff-n-puff), continuous CO₂ injection and water-alternating-CO₂ injection, among which CO₂ huff-n-puff appears to be more efficient to increase heavy oil recovery, though the recovery factor is still low (Sayegh and Maini, 1984; Sahin et al., 2008).

Addition of solvents to the CO₂ stream will generally accelerate the processes of swelling heavy oil and reducing its viscosity, achieving a higher oil recovery in the VAPEX process (Talbi and Maini, 2008). Although some laboratory efforts have been conducted to study the mechanisms for heavy oil recovery by CO₂ injection, it is still not well understood how addition of solvents will affect the CO₂ injection for enhancing heavy oil recovery. Therefore, it is of fundamental and practical importance to study phase behaviour and mass transfer of the solvent(s)-CO₂-heavy oil systems and determine potential of CO₂ cyclic injection in combination with solvents for enhancing oil recovery in such thin heavy oil reservoirs where other processes are not applicable.

1.2 Objective of This Study

The major objective of this proposed research is to provide a pragmatic method and correlations/theoretical models for determining and simulating phase behaviour and
physical properties of solvent(s)-CO$_2$-heavy oil systems for enhanced heavy oil recovery. The detailed objectives are listed as follows,

1) To conduct PVT tests to study phase behaviour of CO$_2$-heavy oil systems and solvent(s)-CO$_2$-heavy oil systems under subcritical and supercritical conditions, respectively;

2) To measure the equilibrium properties including swelling factor, equilibrium interfacial tension (IFT) and molecular diffusion coefficients for the above-mentioned systems; and

3) To develop correlations and/or theoretical models for simulating phase behaviour and mass transfer determined in Objectives #1 and 2.

1.3 Outline of the Dissertation

There are eight chapters in this dissertation. Chapter 1 introduces the research topic together with its major research objectives. Chapter 2 provides an updated literature review on phase behaviour and mass transfer of CO$_2$-heavy oil systems, C$_3$H$_8$-heavy oil systems, and $n$-C$_4$H$_{10}$ heavy oil systems, respectively. Chapter 3 presents a new alpha function in the Peng-Robinson equation of state (PR EOS) to more accurately predict the vapour pressure of non-hydrocarbons and hydrocarbon compounds, respectively. Chapter 4 includes the experimental measurements and theoretical determination of saturation pressures, swelling factors and viscosities of the solvent(s)-CO$_2$-heavy oil systems with the PR EOS. Chapter 5 presents the measured equilibrium interfacial tensions (IFTs) of the solvent(s)-CO$_2$-heavy oil systems together with the mechanical parachor model. Chapter 6 focuses on the measurements made on the liquid-liquid-vapour (L$_1$L$_2$V) three-
phase behaviour of solvent(s)-CO$_2$-heavy oil systems. The measured molecular diffusion coefficients of solvent(s)-CO$_2$-heavy oil systems are discussed in Chapter 7. Finally, conclusions of the current research and recommendation for future work are presented in Chapter 8.
CHAPTER 2  LITERATURE REVIEW

2.1 Immiscible CO₂ Processes

In principle, there exist three categories of CO₂ flooding processes: miscible, near miscible and immiscible (Blunt et al., 1993). Miscible displacement of crude oil by CO₂ is the most desirable scenario that can yield maximum recovery efficiency. This is ascribed to the favourable mechanisms initiated by forming a single-phase containing CO₂ and crude oil through multiple contacts. Oil swelling, oil viscosity reduction, elimination of interfacial tension, and vaporization and extraction of intermediate components from the crude oil all contribute to a low residual oil saturation (Orr and Taber, 1984). In general, minimum miscibility pressure (MMP) is decreased with the API gravity of crude oil (Alston, 1985; Shokir, 2007; Li et al., 2012). As for oil reservoir containing crude oil with 30°API or lower, the MMP would be too high to achieve such that only immiscible state could prevail during CO₂ injection processes in a hydrocarbon reservoir (Mangalsingh and Jagai, 1996).

Although the immiscible CO₂ flooding is a non-thermal recovery method, it shows considerable potential for a range of heavy oil reservoirs. During the immiscible flooding process, CO₂ is injected into the formation, highly mobilizing the oil contacted and displacing it towards the production wells. Oil mobility is improved due to solubility of CO₂ in the oil that causes a reduction in the viscosity, and an increase in oil volume (Al-Abri and Amin, 2010). Recovery mechanisms related to immiscible CO₂ flooding consist of viscosity reduction, oil swelling effect, and interfacial tension reduction.
Viscosity reduction: It is mainly attributed to the dissolution of CO₂ into the crude oil. The viscosity of CO₂ saturated oil is a function of temperature, pressure, and concentration of dissolved CO₂. A decrease in viscosity due to carbonation is generally unimportant for light oils, but plays a significant role in the recovery of heavy oil. For example, when temperature is set at 75°F, the viscosity of a Wilmington oil sample with 15°API is reduced from 2000 cP to 20 cP with pressure increasing from 0 psia to 1500 psia (Spivak and Chima, 1984).

Oil swelling: When CO₂ comes into contact with crude oil, it is expanded due to the dissolution of CO₂. Degree of swelling depends on pressure, temperature, and oil composition. Swelling is important in that the residual oil saturation is inversely proportional to the swelling factor (Hatzignatiou and Lu, 1994; Mangalsingh and Jagai, 1996).

Interfacial tension reduction: Reduction of interfacial tension takes place due to the dissolution of CO₂ into heavy oil. For a heavy oil at moderate pressures (4-6 MPa) and temperature (293.15-298.15 K) with dissolved CO₂ of 50-100 m³/m³, a 30% reduction of interfacial tension can be observed (Kamal, 1986; Mangalsingh and Jagai, 1996). Reduction of interfacial tension increases the capillary number and thus enhances oil recovery.

2.2 Phase Behaviour and Physical Properties

Most of the aforementioned mechanisms associated with immiscible CO₂ flooding depend on the phase behaviour and mass transfer of CO₂-heavy oil systems. Phase behaviour is a critical factor in determining both the displacement efficiency and oil
recovery by CO₂ injection (Orr and Silva, 1983; Orr et al., 2003). The mechanism of CO₂ flooding of heavy oil is complicated by the low temperature usually encountered in heavy oil reservoirs. At a low temperature which is close to 304.19 K (i.e., the critical temperature of CO₂), phase behaviour of liquid (L₁) equilibrium, liquid/vapour (L₁V) equilibrium, liquid/liquid (L₁L₂) equilibrium, and liquid/liquid/vapour (L₁L₂V) equilibrium can take place in CO₂-light oil systems (Orr, 1981; Suehiro et al., 1996). Analogous to a CO₂-light oil system, L₁, L₁V, L₁L₂ and L₁L₂V equilibria have been also observed in CO₂-heavy oil systems (Badamchi-Zadeh et al., 2009).

2.2.1. CO₂-alkane systems

It is necessary to examine the phase behaviour of CO₂ with pure hydrocarbons to better understand the phase behaviour of CO₂-crude oil systems. For an arbitrary binary mixture, nine types of phase diagrams have been identified through either laboratory experiments or theoretical calculations (van Konynenburg and Scott, 1980; Wang and Sadus, 2003). FIGURE 2-1 shows the conceptual layouts of the nine types of phase diagrams.

Phase behaviour of CO₂-alkane systems demonstrates more asymmetrical characteristics with the increase of carbon number of alkanes since the length of alkane chain is extended by adding more carbon atoms. In general, three types of phase behaviour have been observed for CO₂-alkane systems: Types I, II, and III (Liphard and Schneider, 1975; Orr et al., 1981). Mixtures of CO₂ with alkanes from methane up to hexane demonstrate only L₁V equilibria, as indicated by phase diagram of Type I in FIGURE 2-1. For such systems the critical line commences at the critical point of one pure component and moves smoothly to the critical point of the other component as the
FIGURE 2-1: Phase behaviour classification for binary mixtures. Types I, II, III, IV, V and VI behaviour are observed experimentally, whereas behaviour of Types Vm, VII and VIII have only been reported in the literature from calculations. Critical equilibria of the binary mixtures (—), the critical points of the pure components (C), the vapour pressure curves (- - - , 1 and 2) and three-phase liquid-liquid-vapour (-----) equilibria are illustrated. UCEP and LCEP denote upper critical end point (where L2 and V become identical) and lower critical end point (where L1 and L2 become identical), respectively (Wang and Sadus, 2003)
mixture becomes richer in the second component. Mixtures of CO₂ with alkanes from \( n \)-heptane and \( n \)-tridecane (C\(_{13}\)) show \( L_2V \), \( L_1L_2 \) and \( L_1L_2V \) equilibria, as illustrated by phase diagram of Type II in FIGURE 2-1. Type II phase behaviour is slightly more complicated in that there is a \( L_1L_2 \) region at low temperatures and high pressures, while a three phase region \( L_1L_2V \) occurs at low temperatures and low pressures (Sandler, 1999).

Binary mixture of CO₂ and alkane \( n \)-tetradecane (C\(_{14}\)) and heavier illustrates Type III phase behaviour as shown in FIGURE 2-1. Compared to Type II phase behaviour, the \( L_1L_2 \) critical locus moves to a higher temperature and merges with the \( L_2V \) critical locus into a continuous critical curve (Orr \textit{et al.}, 1981). As can be observed from FIGURE 2-1, one vapour-liquid critical line originates at critical point of CO₂ and terminates at the upper-critical-end-point (UCEP), whereas the other starts at critical point of the alkane and then smoothly merges into the \( L_1L_2 \) critical line.

Orr (1984) reported the phase behaviour of CO₂/\( n \)-hexadecane mixtures at 70ºF and 90ºF showing liquid/vapour and liquid/liquid equilibria. As can be seen from FIGURE 2-2, at 70ºF and pressure below about 800 psia, a C\(_{16}\)-rich phase containing dissolved CO₂ is in equilibrium with a vapour that is composed of almost pure CO₂. For the binary mixture of CO₂ and \( n \)-hexadecane, the degree of freedom of three-phase coexistence is 1 according to the Gibbs phase rule,

\[
F = nc - n + 2
\]  \hspace{1cm} [2-1]

where \( nc \) is the number of components in the system and \( n \) is the number of coexisting phases. This indicates that the three-phase locus in the \( P-T \) diagram exists as a line. Thus, three phases can coexist at only one pressure for the binary CO₂-\( n \)-hexadecane at a fixed temperature. At pressure above the three-phase pressure but below the vapour pressure of
FIGURE 2-2: Phase behaviour of CO₂/\(n\)-hexadecane mixtures at 70°F and 90°F showing liquid-vapour and liquid-liquid equilibria (Orr, 1984)
CO₂ (i.e., 855 psia), the L₁L₂ region is separated from the tiny L₂V region by a small single L₂ region. The L₂V region will disappear at the vapour pressure of CO₂, whereas the L₁L₂ region persists to higher pressures. Similar phase behaviour is observed for the binary system at 90°F. It is worthwhile noting that, at a higher temperature, the pressure at which three phases coexist shows a higher value. In addition, it can be observed that in the L₁V region, the solubility of CO₂ in n-hexadecane increases as pressure increases while decreases as temperature increases. The phase behaviour of the binary CO₂-hexadecane system is very useful to understand the phase behaviour of CO₂-heavy oil system since heavy oil is mainly composed of heavy hydrocarbons.

As shown in FIGURE 2-3, Lifhard and Schneider (1975) found that the critical locus of L₁L₂ moves to a higher temperature as the molecular weight of the alkane increases. This observation suggests that the maximum temperature where the L₁L₂ immiscibility can occur in a CO₂-alkane system also increases with the carbon numbers of the alkane. After comparing the phase behaviour of several CO₂-crude oil systems and CO₂-alkane systems, Orr et al. (1981) concluded that oils with a C₄₊ fraction of higher molecular weight would show L₁L₂ behaviour at a higher temperature than oils with a lower molecular weight C₁₄₊ fraction. In the case of heavy oil, the L₁L₂ immiscibility can be expected to exist at a high pressure and elevated temperature. However, the phase behaviour at such a high pressure is of no practical importance to heavy oil recovery since the original pressure of most of the heavy oil reservoirs is fairly low.

2.2.2. CO₂-heavy oil systems

Due to low temperatures and low pressures encountered in most heavy oil reservoirs, it is of more practical significance to study the phase behaviour of CO₂-heavy oil systems
FIGURE 2-3: Phase diagrams of binary CO$_2$-alkane mixtures. Three phase lines are omitted (Liphard and Schneider, 1975)
at low pressures and temperatures. The binary CO\textsubscript{2}-heavy oil system is expected to exhibit Type III phase behaviour, analogous to that of CO\textsubscript{2}-heavy alkane systems with carbon number greater than 13. FIGURE 2-4 illustrates the three-phase co-existing loci for CO\textsubscript{2} and alkanes heavier than C\textsubscript{13} (Larson et al., 1989). As illustrated in FIGURE 2-4, the three-phase loci lie just below the real and extrapolated vapour pressure line of CO\textsubscript{2}. With the increase of carbon number of alkane, the three-phase line tends to move closer to the vapour pressure of CO\textsubscript{2}. The $K$ point at which the L\textsubscript{2} and V phase interface disappears also lies closer to the critical point of CO\textsubscript{2}.

FIGURE 2-5 is a conceptual phase diagram of a pseudo CO\textsubscript{2}-heavy oil system based on phase behaviour of CO\textsubscript{2}-heavy alkane systems. According to the Gibbs phase rule, the coexisting three-phase region is an enclosed area instead of a line. The three-phase region should lie close to the vapour pressure line of CO\textsubscript{2}, while the $K$ point of the CO\textsubscript{2}-heavy oil system should be also close to the critical point of CO\textsubscript{2}. Mehrotra and Svrcek (1984) and Badamchi-Zadeh et al. (2009) experimentally demonstrated the conceptual phase diagram of CO\textsubscript{2}-heavy oil system. Mehrotra and Svrcek (1984) observed a three phase region for the CO\textsubscript{2}-bitumen system at 285.15 K and around 4.5 MPa. The three phases included a liquid phase rich in hydrocarbon, a liquid phase rich in carbon dioxide, and a vapour phase that was essentially filled with CO\textsubscript{2}. Badamchi-Zadeh et al. (2009) discovered that, for a given binary mixture of CO\textsubscript{2} and bitumen, there was a transition zone from liquid-liquid to vapour-liquid-liquid to vapour-liquid phase regimes as the pressure was reduced at a constant temperature below the critical point of pure CO\textsubscript{2}. The $L_1L_2V$ region was narrow, spanning at most 800 kPa (116 psia) at any given temperature. Above the critical point of CO\textsubscript{2}, only two phases were observed at all measured
FIGURE 2-4: Three-phase loci for binary CO$_2$-alkane mixtures (Larson et al., 1989)
**FIGURE 2-5:** Conceptual phase diagrams of a pseudo CO₂-heavy oil system based on phase behaviour of CO₂-heavy alkane systems. Dotted line denotes vapour pressure of CO₂.
temperatures and pressures.

Most of the previous efforts have been devoted to investigating both the \( L_1V \) region (involving subcritical CO\(_2\)) and liquid-fluid (involving supercritical CO\(_2\)) region that take place in CO\(_2\)-heavy oil systems. Solubility of CO\(_2\) in heavy oil or bitumen is usually used as an important index to quantify the maximum amount of CO\(_2\) that can be dissolved in a given amount of heavy oil. Solubility is normally a function of pressure, temperature and oil properties. Data on solubility of subcritical and supercritical CO\(_2\) in light oils or heavy oils under different conditions have been extensively documented in the literature.

TABLE 2-1 lists an exhaustive review of the published data on solubility, density and viscosity of CO\(_2\) in heavy oil or bitumen with API gravity less than 20º. Several major points can be obtained from the studies on phase behaviour of CO\(_2\) with various heavy oils in the literature:

(1) CO\(_2\) cannot achieve miscibility with heavy oil under all the conditions studied;

(2) In general, solubility of CO\(_2\) in heavy oil decreases as temperature increases. At temperatures below the \( K \) point of the CO\(_2\)-heavy oil system, CO\(_2\) solubility increases with pressure but levels off when system pressure reaches a certain point. This observation corresponds to the three-phase \( L_1L_2V \) region or two liquid phase \( L_1L_2 \) region as depicted in Figure 2-4. The corresponding pressure can be either approximated with the CO\(_2\) vapour pressure with temperature lower than its critical temperature or extrapolated its vapour pressure with temperature between its critical temperature and the \( K \) point of the CO\(_2\)-heavy oil system. At temperatures above the \( K \) point of the CO\(_2\)-heavy oil system, solubility of CO\(_2\) in
TABLE 2-1: Phase behaviour of CO₂-heavy oil systems documented in the literature

<table>
<thead>
<tr>
<th>Oil Sample</th>
<th>API @ 60°F</th>
<th>Viscosity, cP</th>
<th>MW g/mol</th>
<th>Temperature °F</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wyoming heavy oil</td>
<td>17.0</td>
<td>600 @ 80°F</td>
<td>N/A</td>
<td>80</td>
<td>Welker and Dunlop, 1963</td>
</tr>
<tr>
<td>A</td>
<td>17.3</td>
<td>87 @ 110°F</td>
<td>350</td>
<td>110, 200</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>D</td>
<td>18.3</td>
<td>74 @ 120°F</td>
<td>358</td>
<td>120, 250</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>E</td>
<td>13.5</td>
<td>1300 @ 120°F</td>
<td>463</td>
<td>120, 200</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>F</td>
<td>12.1</td>
<td>105 @ 120°F</td>
<td>330</td>
<td>120</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>H</td>
<td>11.9</td>
<td>499 @ 130°F</td>
<td>458</td>
<td>130</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>l</td>
<td>18.2</td>
<td>58.6 @ 145°F</td>
<td>370</td>
<td>145</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>Wyoming heavy oil</td>
<td>17.0</td>
<td>800 @ 75°F</td>
<td>N/A</td>
<td>75, 140, 200</td>
<td>Miller and Jones, 1981</td>
</tr>
<tr>
<td>Cat Canyon heavy oil</td>
<td>10.0</td>
<td>4500 @ 140°F</td>
<td>N/A</td>
<td>140, 200</td>
<td>Miller and Jones, 1981</td>
</tr>
<tr>
<td>Wyoming heavy oil</td>
<td>15.0</td>
<td>2000 @ 75°F</td>
<td>N/A</td>
<td>75, 140, 200</td>
<td>Miller and Jones, 1981</td>
</tr>
<tr>
<td>Athabasca bitumen</td>
<td>9</td>
<td>&gt;10000 @ 110.3°F</td>
<td>554.6</td>
<td>73.4-207.32</td>
<td>Mehrotra and Svrcek, 1982</td>
</tr>
<tr>
<td>Marguerite Lake bitumen</td>
<td>N/A</td>
<td>271000 @ 56°F</td>
<td>N/A</td>
<td>53.6-217.4</td>
<td>Mehrotra and Svrcek, 1984</td>
</tr>
<tr>
<td>Peace River bitumen</td>
<td>10.0</td>
<td>14700 @ 104.4°F</td>
<td>542</td>
<td>74.3-224.6</td>
<td>Mehrotra and Svrcek, 1985a</td>
</tr>
<tr>
<td>Athabasca bitumen</td>
<td>9.0</td>
<td>N/A</td>
<td>554.6</td>
<td>212</td>
<td>Fu et al., 1985</td>
</tr>
<tr>
<td>Wabasca bitumen</td>
<td>8.9</td>
<td>8100 @ 55.4°F</td>
<td>446.5</td>
<td>70.52-302.00</td>
<td>Mehrotra and Svrcek, 1985b</td>
</tr>
<tr>
<td>Saskatchewan heavy oil</td>
<td>15.3</td>
<td>2600 @ 68°F</td>
<td>423</td>
<td>82.4</td>
<td>Jha, 1986</td>
</tr>
<tr>
<td>Bartlett heavy oil</td>
<td>16.8</td>
<td>1484.35 @ 75°F</td>
<td>N/A</td>
<td>75, 140, 200</td>
<td>Chung et al., 1988</td>
</tr>
<tr>
<td>Senlac heavy oil</td>
<td>15.0</td>
<td>2600 @ 68°F</td>
<td>N/A</td>
<td>82.31</td>
<td>Quail et al., 1988</td>
</tr>
<tr>
<td>Aberfeldy oil sample 1</td>
<td>17.0</td>
<td>1032 @ 73.4°F</td>
<td>425</td>
<td>73.4</td>
<td>Rojas and Farouq Ali, 1988</td>
</tr>
<tr>
<td>Aberfeldy oil sample 2</td>
<td>14.0</td>
<td>4681 @ 73.4°F</td>
<td>460</td>
<td>73.4</td>
<td>Rojas and Farouq Ali, 1988</td>
</tr>
<tr>
<td>Cold Lake bitumen</td>
<td>N/A</td>
<td>15700 @ 86.9°F</td>
<td>533</td>
<td>59.0-217.4</td>
<td>Mehrotra and Svrcek, 1988</td>
</tr>
<tr>
<td>Cold Lake bitumen</td>
<td>N/A</td>
<td>N/A</td>
<td>533</td>
<td>122-482</td>
<td>Yu et al., 1989</td>
</tr>
</tbody>
</table>
TABLE 2-1: Phase behaviour of CO₂-heavy oil systems documented in the literature (continued)

<table>
<thead>
<tr>
<th>Oil Sample</th>
<th>API @ 60ºF</th>
<th>Viscosity, cP</th>
<th>MW, g/mol</th>
<th>Temperature, ºF</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peace River bitumen</td>
<td>10.0</td>
<td>14700 @ 104.4ºF</td>
<td>542</td>
<td>58.46-234.86</td>
<td>Mehrotra and Svrcek, 1989</td>
</tr>
<tr>
<td>Peace River bitumen</td>
<td>10.0</td>
<td>14700 @ 104.4ºF</td>
<td>542</td>
<td>175.3-391.8</td>
<td>Svrcek et al., 1989</td>
</tr>
<tr>
<td>Lindbergh heavy oil</td>
<td>14.7</td>
<td>12086 @ 69.8ºF</td>
<td>490</td>
<td>69.8-284</td>
<td>Sayegh et al., 1990</td>
</tr>
<tr>
<td>Athabasca bitumen</td>
<td>8.9</td>
<td>10000 @ 121ºF</td>
<td>640</td>
<td>185.1, 248.1</td>
<td>Deo et al., 1991</td>
</tr>
<tr>
<td>Tar Sand Triangle bitumen</td>
<td>8.9</td>
<td>10000 @ 140.3ºF</td>
<td>701</td>
<td>185.1, 248.2</td>
<td>Deo et al., 1991</td>
</tr>
<tr>
<td>PR Spring bitumen</td>
<td>8.0</td>
<td>100000 @ 161.3ºF</td>
<td>541</td>
<td>185.1, 248.3</td>
<td>Deo et al., 1991</td>
</tr>
<tr>
<td>Suffield heavy oil</td>
<td>17.0</td>
<td>685 @ 69.8ºF</td>
<td>358</td>
<td>68-284</td>
<td>Kodal and Sayegh, 1992</td>
</tr>
<tr>
<td>West Sak heavy oil 1</td>
<td>18.5</td>
<td>241.5 @ 75ºF</td>
<td>330</td>
<td>65</td>
<td>DeRuiter et al., 1994</td>
</tr>
<tr>
<td>West Sak heavy oil 2</td>
<td>14.0</td>
<td>5243.7 @ 75ºF</td>
<td>446</td>
<td>60</td>
<td>DeRuiter et al., 1994</td>
</tr>
<tr>
<td>Aberfeldy oil</td>
<td>17.0</td>
<td>1050 @ 73.4ºF</td>
<td>N/A</td>
<td>73.4</td>
<td>Nguyen and Farouq Ali, 1998</td>
</tr>
<tr>
<td>Jiangsu heavy oil</td>
<td>N/A</td>
<td>N/A</td>
<td>384</td>
<td>131, 167</td>
<td>Liu et al., 1999</td>
</tr>
<tr>
<td>Senlac heavy oil</td>
<td>14.1</td>
<td>3580 @ 68ºF</td>
<td>440</td>
<td>82.4</td>
<td>Srivastava et al., 1999</td>
</tr>
<tr>
<td>Athabasca bitumen</td>
<td>9.0</td>
<td>&gt;10000 @ 110.3ºF</td>
<td>552</td>
<td>77</td>
<td>Badamchi-Zadeh et al., 2009</td>
</tr>
</tbody>
</table>

Note:
a: These designations were used in the original literature

MW: Molecular weight
heavy oil increases with pressure and no level-off phenomenon has been reported in the literature;

(3) The effect of CO₂ solubility on the density of CO₂-saturated heavy oil or bitumen is ambiguous. This may be explained by the fact that an increase of pressure leads to a volume increase of heavy oil but compresses the volume at the same time;

(4) The swelling factor increases with CO₂ solubility in heavy oil and shows its highly linear relationship (Welker and Dunlop, 1963; Chung et al., 1988); and

(5) The viscosity of heavy oil saturated with CO₂ decreases dramatically with CO₂ solubility. It is worth noting that the decline trend normally terminates when the three-phase or two-liquid phase region is encountered and begins to level off afterwards. In addition, effect of viscosity reduction caused by CO₂ dissolution is more pronounced for heavy oils than that of light oils. In some scenarios as observed by Chung et al. (1988), dissolution of CO₂ is even capable of reducing viscosity of heavy oil more than heating the heavy oil.

Interfacial tension is another important physical property that affects CO₂ flooding efficiency (Yang and Gu, 2005). A reduced interfacial tension of heavy oil due to CO₂ dissolution is favourable for increasing heavy oil recovery since the capillary number is increased with the reduced interfacial tension. Yang and Gu (2006) measured the change of equilibrium interfacial tension with pressure at 298.15 K for a CO₂-Ontario heavy oil system. It was found that the interfacial tension decreases linearly with the pressure in the tested pressure range. As mentioned previously, at pressure lower than L₁L₂ or L₁L₂V pressure of the CO₂-heavy oil system, the solubility of CO₂ in heavy oil increases with
saturation pressure. The dissolved CO$_2$ functions as a surface-active agent, which is responsible for the interfacial reduction (Yang and Gu, 2006).

2.3 Correlations for Physical Properties

Physical properties of CO$_2$-heavy oil system, including CO$_2$ solubility, swelling factor, density, and viscosity are of great importance for designing a successful CO$_2$ immiscible flooding project in a heavy oil reservoir. In the literature, many correlations have been documented to predict the physical properties of CO$_2$-light oil systems, only some of which are specially designed for CO$_2$-heavy oil systems.

2.3.1. CO$_2$ solubility

Welker and Dunlop (1963) studied the physical properties of several light oils and heavy oils saturated with CO$_2$ at 80°F. They graphically expressed the CO$_2$ solubility as a function of saturation pressure and API gravity. It was the first attempt to provide correlations regarding CO$_2$ solubility in light and heavy oils. Similarly, Simon and Graue (1964) conducted a comprehensive study of phase behaviour of CO$_2$ with nine crude oil samples including six heavy oil samples, resulting in graphical correlations in which CO$_2$ solubility is expressed as a function of saturation pressure, temperature and the UOP (Universal Oil Product) characterization factor. These graphical correlations have been widely used in the petroleum industry since their development. However, such correlations are expressed in a graphical form, which is not convenient for computer calculations or reservoir simulation studies.
Mehrotra and Svrcek (1982) presented an empirical correlation for CO₂ solubility in bitumen based on the experimental results as below,

\[
R_s \left( \frac{m^3}{m^3} \right) = a_1 + a_2P + a_3 \left( \frac{P}{T} \right) + a_4 \left( \frac{P}{T} \right)^2
\]

[2-2]

where \( R_s \) is volumetric solubility of CO₂ in bitumen, \( P \) is saturation pressure, \( T \) is temperature, and \( a_1 - a_4 \) are empirical constants. Note that the saturation pressure should be less than or equal to the vapour pressure of CO₂ at temperature lower than the critical point of CO₂.

Chung et al. (1988) provided a correlation for solubility of CO₂ in heavy oil in the following form,

\[
R_s \left( \frac{scf}{bbl} \right) = \frac{1}{b_1 \gamma^b T^{b_5} + b_2 T^{b_5} \exp \left( -b_6P + \frac{b_7}{P} \right)}
\]

[2-3]

where \( b_1 - b_7 \) are empirical constants.

Emera and Sarma (2006) developed correlations to predict CO₂ solubility, oil swelling factor, CO₂-oil density and CO₂-oil viscosity for both light or heavy oils using a genetic algorithm (GA)-based technique. Their correlations recognized not only all major parameters that affect each physical property, but also took into account the effects of CO₂ liquefaction pressure and oil molecular weight (MW). For temperatures greater than the critical temperature of CO₂ (for all pressures) and temperatures less than critical temperature of CO₂ (for pressures less than CO₂ L₁L₂ and L₁L₂V phase pressure),

\[
R_s \left( \text{mole } \% \right) = c_1 + c_2 y + c_3 y^{c_5} + c_4 y^{c_6}
\]

[2-4]

where
\[ y = SG\left[\frac{\sum T}{P}\right]^{\exp\left(\frac{y_{MW}}{PT}\right)} \]  

where \( c_1 - c_7 \) are empirical constants and \( SG \) is the oil specific gravity. They also presented solubility correlation for pressures greater than three-phase or liquid-liquid phase pressure of a \( \text{CO}_2 \)-oil system. According to this correlation, solubility of \( \text{CO}_2 \) will increase further with system pressure. According to TABLE 2-1, it has been found that the solubility of \( \text{CO}_2 \) in heavy oil may keep unchanged or even decrease with pressure that is greater than the \( L_1L_2 \) and \( L_1L_2V \) phase pressure of the \( \text{CO}_2 \)-oil system. Therefore, it is not recommended to use the correlation developed by Emera and Sarma (2006) for this pressure range, whereas a constant \( \text{CO}_2 \) solubility in heavy oil is recommended.

Based on the simplified Henry’s Law, Badamchi-Zadeh et al. (2009) obtained a correlation for \( \text{CO}_2 \) solubility in crude oil based on the data of Simon and Graue (1964),

\[ R_s (\text{mole \%}) = \frac{P}{H_{\text{CO}_2}} = \frac{P}{\ln d_1 + \frac{d_2}{T} + \frac{d_3 P}{RT}} \]  

where \( H_{\text{CO}_2} \) is Henry’s constant at \( T \), \( R \) is universal gas constant, \( d_1-d_3 \) are empirical constants. Their correlation is claimed to fit well with the experimental data with absolute average error of 1.7%.

Another approach adopted in the literature is to use the cubic equation of state (CEOS) to correlate the experimental data on \( \text{CO}_2 \) solubility in heavy oil. Fu et al. (1985) treated bitumen as a single pseudocomponent and used the PR EOS to reproduce the solubility data with good accuracy. The similar methodology had also been adopted by Jamaluddin et al. (1991) to successfully reproduce the solubility of \( \text{CO}_2 \) in eleven heavy oil or bitumen samples and the density data of these systems with a different EOS.
Kariznovi et al. (2010) used six universal pseudocomponents that are optimized to characterize Alberta bitumen, which are independent of bitumen type and can be used in the PR EOS to predict the solubility of CO₂ in Alberta bitumen (Athabasca, Wabasca, Peace River, and Cold Lake) with satisfactory accuracy. Their results also showed that the Lee-Kesler correlation was the most appropriate correlation for CO₂-bitumen systems to determine the critical properties of the pseudocomponents.

2.3.2. Swelling factor

According to Welker and Dunlop (1963), swelling factor is defined as the volume of crude oil saturated with CO₂ at reservoir pressure and temperature divided by the volume of crude oil at atmospheric pressure (0.1 MPa) and reservoir temperature. This definition has become a norm in the petroleum industry since its introduction. The swelling of heavy oil is mainly attributed to the dissolution of CO₂ into oil. Thereby, a strong dependence of swelling factor on solubility is expected. Welker and Dunlop (1963) provided a correlation for swelling factor as a function of CO₂ solubility,

\[ SF = 1.0 + \frac{0.35R_s}{1000} \]  \[2-7\]

where \( SF \) is swelling factor, and \( R_s \) is CO₂ solubility in scf/bbl. Chung et al. (1988) measured the swelling factors of four different heavy oils saturated with CO₂. Equation [2-7] provides a fairly good fit to their experimental data, suggesting a strong linear relationship between swelling factor and solubility for heavy oil. Simon and Graue (1964) devised a graphical correlation for predicting swelling factor of different crude oil saturated with CO₂. In order to eliminate the inconvenience brought along by the graphical representation of swelling factor correlation, Emera and Sarma (2006)
developed a expression for swelling factor as a function of oil molecular weight and CO₂ solubility based on the experimental data including those of Simon and Graue (1964).

Since the Simon-Graue correlations are completely empirical and lack of theoretical basis, the extrapolation outside their range or extension to other systems is expected to introduce a large error. The EOS modelling is a possible approach to calculate swelling factor of CO₂ saturate oil. It has been shown by Teja and Sandler (1980) that the swelling factor can be calculated by molar volume and molar solubility in the following form,

\[ SF = \frac{V_{s2}}{V_{s1}} \times \frac{1}{1 - X} \] 

[2-8]

where \( V_{s1} \) is the molar volume of CO₂ saturated oil at saturation temperature and atmospheric pressure, \( V_{s2} \) is the molar volume of CO₂ saturated oil at saturation temperature and saturation pressure, and \( X \) is the CO₂ solubility in mole fraction.

Mullken and Sandler (1980) treated the crude oil as a single pseudocomponent and characterized it with specific gravity and normal boiling point or Watson \( K \) factor. They firstly calculated the solubility of CO₂ in crude oil and density of the mixture using PR EOS and then obtained the swelling factor of CO₂ saturated oil based on Equation [2-8]. Such a method showed comparable accuracy compared to the graphical correlations of Simon and Graue (1964), while a binary interaction parameter (BIP) formula was obtained by regressing the CO₂ solubility data,

\[ \delta = 0.5010 - 0.3576T_r - 0.18285SG - 0.0961\omega \] 

[2-9]

where \( \delta \) is BIP between CO₂ and oil, \( T_r \), \( SG \), and \( \omega \) are reduced temperature, specific gravity and acentric factor of crude oil, respectively, which are calculated from the Lee-Kesler correlation.
2.3.3. Viscosity

Viscosity is an important parameter to characterize the flowing property of heavy oil. Significant reduction of heavy oil viscosity after being saturated with CO₂ has been extensively documented in the literature. Since it is extremely difficult to quantify the individual contribution of each component in heavy oil to the viscosity of the mixture, CO₂-heavy oil mixture is usually treated as a pseudo-binary system with two components: CO₂ and heavy oil. Viscosity of CO₂-heavy oil mixtures is generally a function of the mixture composition. The viscosity reduction degree of heavy oil is dependent on how much CO₂ is dissolved in the heavy oil. Therefore, if the concentration of CO₂ in the crude oil and viscosities of CO₂ and heavy oil are known, a correlation can be developed to predict the viscosity of CO₂-heavy oil mixtures. According to Chung et al. (1988), the viscosity ratio of heavy oil to CO₂ falls in the range of $10^3$ to $10^6$. Several correlations have been developed for estimating the viscosity of solvent-solute mixture with such large viscosity ratios.

Based on the fact that the mixture viscosity is not a simply linear function of the solvent fraction, Cragoe (1933) developed a widely used method for liquid mixture viscosity predictions. Mixing rules are used in their model to combine the “Liquidity” $L$ of the solvent and solute. Liquidity is expressed as,

$$L = \frac{1000 \ln 20}{\ln \mu - \ln(5 \times 10^{-4})} \quad [2-10]$$

where $\mu$ is the viscosity of the solvent or solute. The mixture liquidity is calculated from the following mixing rule,

$$L_m = w_1 L_1 + (1 - w_1) L_2 \quad [2-11]$$
where $L_m$ is mixture liquidity, $w_1$ is the weight fraction of solvent in the mixture, $L_1$ and $L_2$ are the liquidity of solvent and solute, respectively. Then the mixture viscosity can be calculated by Equation [2-10]. The Cragoe correlation can be used for calculating the viscosity of heavy oil saturated with CO$_2$. However, the weight fraction of CO$_2$ should be known prior to calculation.

Lederer (1933) presented an equation for mixture viscosity which was modified from the classic Arrhenius expression,

\[
\ln \mu = x_s \ln \mu_s + (1-x_s) \ln \mu_o \quad [2-12a]
\]

and

\[
x_s = \frac{\alpha V_s}{\alpha V_s + V_o} \quad [2-12b]
\]

where $\mu$ is mixture viscosity, $\mu_s$ is solvent viscosity, $\mu_o$ is oil viscosity, $V_s$ and $V_o$ are volume fraction of solvent and oil in the mixture, and $\alpha$ is an empirical constant having a value in the range of 0 to 1. It had been shown by Rahmes and Nelson (1948) that the Lederer correlation exhibited an excellent fit to their experimental data for systems of 26 blends of 17 petroleum fractions.

Shu (1984) extended the Lederer equation to higher viscosity ratios by using a generalized expression for the empirical constant $\alpha$ which is expressed as a function of the component viscosities and densities on the basis of the experimental data for mixtures of heavy oils with light petroleum fractions,

\[
\alpha = 17.04 \left( \frac{\rho_o - \rho_s}{\rho_o^{0.5237} \rho_s^{3.2745}} \right)^{1.6316} \ln \left( \frac{\mu_o}{\mu_s} \right) \quad [2-13a]
\]
where $\rho_s$ and $\rho_o$ are specific gravity of the solvent and heavy oil, respectively. This correlation was tested with heavy oil/bitumen-solvent blending data and provided an excellent prediction of the mixture viscosities. However, the correlation developed by Shu is based on organic solvents (e.g., kerosene) and cannot be applied for CO$_2$-heavy oil systems where CO$_2$ density may be higher than heavy oil density at high pressures. Chung et al. (1988) obtained a modified $\alpha$ correlation that was a function of temperature ($T$ in °R), pressure ($P$ in psia) and specific gravity ($SG$) of heavy oil,

$$\alpha = 0.225SG^{-4.16} \left( \frac{T}{547.57} \right)^{1.85} \left[ \frac{e^{7.36} - e^{7.36\left(1-P/\rho_{\text{oil}}\right)}}{e^{7.36} - 1} \right]$$

[2-13b]

Equations [2-12] and [2-13b] generated excellent reproduction of the viscosity data of CO$_2$-heavy oil mixture for four heavy oils. It is worth noting that EOS is able to provide information on volume fraction of CO$_2$ in heavy oil, which is needed prior to calculating mixture viscosity by using Equations [2-12] and [2-13b].

Obviously, EOS modeling of CO$_2$-heavy oil systems provides an integrated method for predicting CO$_2$ solubility, mixture density, swelling factor, and even mixture viscosity. Therefore, it is important to study phase behaviour of CO$_2$-heavy oil systems and numerical simulating CO$_2$ flooding of heavy oil by conducting EOS modeling.

### 2.4 Phase Behaviour of Solvent(s)-Heavy Oil Systems

It has been found that a gas solvent with a higher critical temperature and boiling point is more soluble than the one with a lower critical temperature, for the vapour pressure is lower for the former, which leads to an increased nonvolatility (Hildebrand,
1936). FIGURE 2-6 shows the vapour pressure lines and critical point of six gas solvents N₂, CH₄, CO₂, C₂H₆, C₃H₈ and n-C₄H₁₀. The nonvolatility of the pure gas solvent is increased with the vapour pressure line moving to the right side of FIGURE 2-6. Then the ranking of solubility of the gas solvents in a given solute shown in FIGURE 2-6 is supposed to follow the order: N₂<CH₄<CO₂<C₂H₆<C₃H₈<n-C₄H₁₀.

As for a CO₂-based solvent flooding process for heavy oil recovery, the promising solvent additives appear to be C₃H₈ and n-C₄H₁₀. This may be accounted for by two major considerations. These two solvents show a much lower nonvolatility, implying a high solubility in heavy oil. On the other hand, they demonstrate a relatively large vapour pressure, enabling the CO₂-solvent(s) mixture to exist in the gas state under reservoir conditions. Therefore, it is meaningful to review the phase behaviour of C₃H₈-heavy oil or n-C₄H₁₀-heavy oil system. Rather than directly running into the phase behaviour of solvent(s)-heavy oil systems, the phase behaviour of short-chain alkane and long-chain alkane system will be firstly covered in the following discussion.

2.4.1. Short-chain alkane and long-chain alkane system

The phase behaviour of short-chain alkane (normally CH₄, C₂H₆, C₃H₈, or n-C₄H₁₀) and long-chain alkane systems has been an intensive research topic which is of great interests to various industry applications. Similar to the CO₂-alkane systems, the homologous alkane-alkane series show a classical transition between different types of phase behaviour (See FIGURE 2-1). The binary mixture of methane and alkane up to n-entane demonstrates Type I phase behaviour (Rowlinson and Swinton, 1982). Partial miscibility in the liquid state appears first in the mixture of methane and n-hexane and a change from Type I phase behaviour to Type V occurs. When the n-alkane
FIGURE 2-6: Vapour pressure lines of six gases $N_2$, $CH_4$, $CO_2$, $C_2H_6$, $C_3H_8$ and $n-C_4H_{10}$. Bold dots denote the critical points (Lide, 2009)
chain length increases, the phase behaviour becomes more complicated. The global phase behaviour of methane and \(n\)-heptane system shows a Type III phase behaviour (Aparicio-Martínez and Hall, 2007).

Analogous to the methane-alkane mixture, the global phase behaviour of a binary \(\mathrm{C}_2\mathrm{H}_6\)-alkane mixture changes from a Type I pattern to a Type V and then to a Type III as the carbon number of alkane increases. According to the experimental observation of Specovius \textit{et al.} (1981), the phase behaviour changing from Type I to Type V happens first for \(n\)-octadecane. The phase behaviour for binary systems of alkanes heavier than \(\mathrm{CH}_4\) or \(\mathrm{C}_2\mathrm{H}_6\) is analogous to that of \(\mathrm{CH}_4\)-alkane system and \(\mathrm{C}_2\mathrm{H}_6\)-alkane system, respectively. These mixtures show Type I behaviour for the lower members of the series, and a Type V transition range appears when carbon number reaches a certain value. Then a Type III phase behaviour occurs with the further increase of carbon number.

Based on experimental observation, Peters \textit{et al.} (1989) estimated that partial miscibility in the liquid state appeared first in the mixture of \(\mathrm{C}_3\mathrm{H}_8\) and alkanes with carbon number between 29 and 30. In addition, binaries of short and long alkanes first showing partial miscibility in the liquid phase has been characterized by their carbon numbers (see FIGURE 2-7) by Peters \textit{et al.} (1989). It can be seen from this figure that a linear relationship between the carbon numbers of solvent and solute exists. According to FIGURE 2-7, a carbon number of 42 can be expected for the binary alkane mixture involving \(n\)-\(\mathrm{C}_4\mathrm{H}_{10}\). The appearance of partial miscibility implies that the solubility of one lighter alkane solvent in one heavier alkane solute is decreased.

Phase behaviour of a binary system of heavy alkane with \(\mathrm{C}_3\mathrm{H}_8/n\)-\(\mathrm{C}_4\mathrm{H}_{10}\) is helpful to interpret the phase behaviour of \(\mathrm{C}_3\mathrm{H}_8/n\)-\(\mathrm{C}_4\mathrm{H}_{10}\) and heavy oil system. Since heavy oil is
FIGURE 2-7: Binaries of short and long \( n \)-alkanes first showing partial miscibility in the liquid phase characterized by their carbon numbers (Peters \textit{et al.}, 1989)
mainly composed of heavy hydrocarbons, the pseudo binary system of $C_3H_8/n-C_4H_{10}$ and heavy oil may exhibit Type III or V pattern.

### 2.4.2. $C_3H_8/n-C_4H_{10}$ with heavy oil

Phase behaviour study of binary system of heavy oil and solvent (including $C_3H_8$ and $n-C_4H_{10}$) is of great importance to the solvent-based heavy oil recovery methods, for example, the solvent flooding process and vapour extraction (VAPEX) process (Upreti et al., 2007). Analogous to CO$_2$-heavy oil systems, complex phase behaviours, for example, $L_1L_2V$ equilibrium, can also take place under certain circumstances as depicted in FIGURE 2-4. However, no $L_1L_2V$ equilibrium has been reported in the literature for the aforementioned systems. TABLE 2-2 lists a review of the published data on phase behaviour of $C_3H_8/n-C_4H_{10}$ and heavy oil systems.

Badamchi-Zadeh et al. (2009a) provided a correlation for $C_3H_8$ solubility in Athabasca bitumen by using a modified Raoult’s Law,

$$x_{C_3} = \frac{P}{1.158p_{C_3}'}$$

where $x_{C_3}$ is $C_3H_8$ solubility in the bitumen in mole fraction, $P$ is saturation pressure of the $C_3H_8$-bitumen system in kPa, and $p_{C_3}'$ is $C_3H_8$ vapour pressure in kPa. Equation [2-14] fits the saturation pressures with an average relative deviation of 5.1%.

### 2.5 Phase Behaviour of Solvent(s)-CO$_2$-Heavy Oil Systems

Although some laboratory efforts have been conducted to study the mechanisms for enhancing heavy oil recovery by CO$_2$ injection (Simon et al., 1978; Klins and Farouq Ali,
TABLE 2-2: Phase behaviour of solvent(s)-heavy oil systems documented in the literature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>MW g/mol</th>
<th>Specific gravity</th>
<th>Temperature °F</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peace River bitumen</td>
<td>C₃H₈</td>
<td>537</td>
<td>1.013</td>
<td>69.8-95</td>
<td>Das and Butler, 1996</td>
</tr>
<tr>
<td>Peace River bitumen</td>
<td>n-C₄H₁₀</td>
<td>537</td>
<td>1.013</td>
<td>95</td>
<td>Das and Butler, 1996</td>
</tr>
<tr>
<td>Fengcheng bitumen</td>
<td>C₃H₈</td>
<td>503</td>
<td>N/A</td>
<td>381</td>
<td>Han et al., 1998</td>
</tr>
<tr>
<td>Winter heavy oil</td>
<td>C₃H₈</td>
<td>412</td>
<td>0.973</td>
<td>59-82.4</td>
<td>Freitag et al., 2005</td>
</tr>
<tr>
<td>Lloydminster heavy oil</td>
<td>C₃H₈</td>
<td>432</td>
<td>0.988</td>
<td>68-75.2</td>
<td>Luo et al., 2007; Luo and Gu, 2009</td>
</tr>
<tr>
<td>Athabasca bitumen</td>
<td>C₃H₈</td>
<td>552</td>
<td>1.007</td>
<td>50-122</td>
<td>Badamchi-Zadeh et al., 2009</td>
</tr>
<tr>
<td>Frog Lake heavy oil</td>
<td>n-C₄H₁₀</td>
<td>400</td>
<td>0.989</td>
<td>233.6-257</td>
<td>Yazdani and Maini, 2010</td>
</tr>
</tbody>
</table>
few attempts have been made to evaluate the phase behaviour and physical properties of the solvent(s)-CO₂-heavy oil systems under subcritical and supercritical conditions (Badamchi-Zadeh et al., 2009a; b). Nevertheless, some investigations have been made to study phase behaviour of ternary solvent-CO₂-alkane systems. Phase behaviour of CO₂-C₃H₈-\(n\)-hexadecane system were reported by Stewart and Nielsen (1954) and Meldrum and Nielsen (1955). Complex phase behaviour took place for the ternary CO₂-C₃H₈-\(n\)-hexadecane system. The three-phase coexisting region was found to expand to a larger region in the \(P-T\) diagram due to the addition of C₃H₈. Similar observation was also reported by Fall and Luks (1986). They reported the phase equilibria data for two ternary systems, i.e., CO₂-C₃H₈-\(n\)-hexadecane system and CO₂-N₂-\(n\)-hexadecane system. As shown in FIGURE 2-8, addition of nitrogen to CO₂-\(n\)-nonadecane resulted in a three-phase region developing to the low-temperature and high-pressure side of the binary \(L_1L_2V\) locus of CO₂-\(n\)-nonadecane system, while addition of C₃H₈ causes the three-phase region to extend to the high-temperature side of the \(L_1L_2V\) locus.

Nguyen and Farouq Ali (1998) studied the effect of nitrogen on CO₂ solubility in Aberfeldy heavy oil and discovered that, even if the partial pressure of CO₂ in a CO₂-N₂ mixture was equal to the pressure of pure CO₂ system, CO₂ solubility in the gas mixture was lower than the pure CO₂ solubility. For pure CO₂, its critical temperature and normal boiling point are 304.19 K and 194.67 K, respectively (Yaws, 2003). For the mixture (\(x(\text{CO}_2)=0.9,\ x(\text{N}_2)=0.1\)), the critical temperature and normal boiling point are about 286.35 K and -183.09K, respectively. Comparing pure CO₂ and CO₂-N₂ mixture, it
FIGURE 2-8: Critical loci for the $L_1L_2V$ regions of the systems of $CO_2-N_2-n$-nonadecane and $CO_2-C_3H_8-n$-nonadecane. Q refers to the point where four-phase solid-liquid-liquid-vapour equilibrium coexists. The solid line denotes the three-phase coexisting line for $CO_2-n$-nonadecane system (Fall and Luks, 1986)
is obvious that pure CO₂ has a higher critical temperature and boiling point than the CO₂-
N₂ mixture. As discussed previously, a gas with a higher critical temperature and boiling point temperature is more soluble than the one with a lower critical temperature. This discussion also implies that addition of more soluble solvents including C₃H₈ or n-C₄H₁₀ to CO₂ stream is expected to result in an increased solubility of the mixture in heavy oil than that of pure CO₂ because C₃H₈ and n-C₄H₁₀ have higher critical temperatures and boiling point temperatures than CO₂.

Talbi and Maini (2008) have shown that addition of solvents including C₃H₈ and n-C₄H₁₀ can generally accelerate the processes of swelling heavy oil and reducing its viscosity in the VAPEX process to a larger extent than pure CO₂. Badamchi-Zadeh et al. (2009b) measured the saturation pressures of CO₂ and C₃H₈ in Athabasca bitumen as well as the liquid-phase densities and viscosities for three ternary CO₂-C₃H₈-bitumen mixtures at temperatures from 283.15 K to 298.15 K. In addition to the observed L₁V phase equilibria and L₁L₂ phase equilibria, L₁L₂V phase equilibria have also been observed in the C₃H₈-CO₂-heavy oil systems. The liquid-phase viscosity of two C₃H₈-CO₂-bitumen mixtures was also presented and suggested that the ternary mixture with a larger concentration of C₃H₈ exhibits a greater viscosity reduction effect.

The existence of three-phase equilibria impose a significant impact on the displacing efficiency of heavy oil since the relative permeability curves can be largely altered due to the presence of multiple phases. Recent studies show, as for CO₂-light oil systems, L₁L₂V phase behaviour is a critical mechanism for achieving high displacement efficiency (Okuno et al., 2011). With regard to the solvent(s)-CO₂-heavy oil systems, how the L₁L₂V phase behaviour affects the recovery performance is still not well understood.
Several important mechanisms can come into play when $L_1L_2V$ phase behaviour appears in the porous media. The heavy oil is diluted and swollen by solvent(s) and CO$_2$ in the $L_1$ phase with a low viscosity, which is beneficial for improving heavy oil recovery. The existence of $L_2$ phase can impose double-sided effect on the *in situ* fluid flow in porous media. On one hand, the $L_2$ phase is more movable in the porous media with a lower viscosity in comparison to the $L_1$ phase and can be easily recovered from the production end (Talbi and Maini, 2008). On the other hand, one possible benefit arising from emergence of the $L_2$ phase is that the $L_2$ phase reduces the gas-phase saturation in the pores. A reduction in gas saturation suppresses the gas-phase relative permeability, hence delays the gas breakthrough and results in a better sweeping efficiency (Feizabadi *et al.*, 2012).

Addition of alkane solvents to the CO$_2$ stream generally accelerates the processes of swelling heavy oil, reducing its viscosity, and decreasing the IFT between heavy oil and CO$_2$, and thus leading to a higher oil recovery in the vapor extraction (VAPEX) process (Talbi and Maini, 2008). Most recently, the synergetic mechanisms of solvent(s)-enriched CO$_2$ flooding are proved by both linear and radial coreflooding experiments with using CO$_2$ only and C$_3$H$_8$-enriched CO$_2$ stream, respectively. Compared to the pure CO$_2$ flooding process, a significantly higher heavy oil recovery factor, as well as less solvent consumption, can be achieved with the C$_3$H$_8$-enriched CO$_2$ flooding process (Luo *et al.*, 2012).

**2.6 Mass Transfer of Solvent(s)-CO$_2$-Heavy Oil Systems**

The foregoing sections of this chapter have been focused on discussing the phase
behaviour of solvent(s)-CO$_2$-heavy oil systems and equilibrium physical properties. Intrusive forces, e.g., the shearing force caused by the rotation of a magnetic stirrer in a typical PVT setup, can be applied to significantly accelerate the mass transfer between solvent(s)-CO$_2$ mixture and heavy oil. However, it takes a long time for the solvent(s)-CO$_2$ mixture to reach equilibrium \textit{in situ} with heavy oil during a huff-n-puff process. It is found that the solvent(s)-CO$_2$ mixture naturally dissolves into heavy oil in a reservoir, making the swollen heavy oil less viscous and hence more mobile (Qazvini Firouz and Torabi, 2012). During dissolution of the solvent(s)-CO$_2$ mixture into heavy oil, the molecular diffusion coefficients can be used to quantify the mass transfer rate of solvent(s)-CO$_2$ mixture into heavy oil.

In the literature, several methods have been developed and applied to determine the molecular diffusion coefficient of a pure gas in heavy oil. These methods include the pressure decay method (Zhang \textit{et al.}, 1999; Upreti and Mehrotra, 2000; Upreti and Mehrotra, 2002; Tharanivasan \textit{et al.}, 2006), volume decay method (Jamialahmadi \textit{et al.}, 2006), constant-pressure technique (Etminan \textit{et al.}, 2010), dynamic pendant drop shape analysis (DPDSA) (Yang and Gu, 2006a), dynamic interfacial tension method (Yang \textit{et al.}, 2006; Yang and Gu, 2008), and microfluidic method (Fadaei \textit{et al.}, 2011). Some methods are developed by recording the gas phase parameters, e.g., pressure (Zhang \textit{et al.}, 1999; Upreti and Mehrotra, 2000; Upreti and Mehrotra, 2002; Tharanivasan \textit{et al.}, 2006) or volume (Jamialahmadi \textit{et al.}, 2006), while the other are focused on monitoring the swelling of heavy oil due to gas dissolution (Yang and Gu, 2006a; Fadaei \textit{et al.}, 2011). The pressure decay method is the most commonly used and non-intrusive method to determine the molecular diffusion coefficient of a pure gas in heavy oil because it reflects
the actual molecular diffusion process with the absence of any exterior forces, though oil swelling is normally neglected. Accordingly, such determined diffusion coefficient may become less accurate because oil swelling can be significant during the diffusion of a gas mixture into heavy oil, in particular, at a high pressure. During the diffusion process, not only does the system pressure decrease, but also the gas-phase volume decreases due to the swelling of the liquid phase. It is desirable to simultaneously monitor both pressure- and volume-history of either gas or liquid phase for more accurate determination of the molecular diffusion coefficient.

Although all the aforementioned methods are suitable for estimating the apparent molecular diffusion coefficient in the case of a gas mixture diffusing into heavy oil, they cannot be used to determine the individual molecular diffusion coefficient of each component in the gas mixture. For example, as for the constant-pressure method, it has been found that the addition of nitrogen into CO$_2$ reduces the apparent gas diffusivity in heavy oil (Nguyen and Farouq Ali, 1998). As for the DPDSA method, the addition of C$_3$H$_8$ into CO$_2$ is found to increase the apparent gas diffusivity in heavy oil (Yang and Gu, 2006). However, the individual contribution of each component in the gas mixture to the bulk diffusion cannot be quantified with the aforementioned methods. Compositional measurements of the gas phase must be carried out before the diffusion test and after the diffusion test to determine individual molecular diffusion coefficients of different gases in heavy oil, thus enabling the evaluation of preferential diffusion of different gases into heavy oil.

It is of fundamental and practical importance to perform further research on phase behaviour and mass transfer of solvent(s)-CO$_2$-heavy oil systems due to the scarcity of
experimental data for these systems as well as accurate theoretical foundations. The scientific findings will provide fundamental data and important insights for designing solvent-assisted CO\textsubscript{2} flooding processes for enhancing heavy oil recovery.

**2.7 Summary**

The following summary can be made from the previous discussions:

1) CO\textsubscript{2}-heavy oil system can exhibit complex phase behaviour including L\textsubscript{1}, L\textsubscript{1}V, L\textsubscript{1}L\textsubscript{2}, L\textsubscript{1}L\textsubscript{2}V equilibria;

2) Solubility of CO\textsubscript{2} in heavy oil decreases as temperature increases. At temperatures below the $K$ point of the CO\textsubscript{2}-heavy oil system, CO\textsubscript{2} solubility increases with pressure but levels off when system pressure reaches a L\textsubscript{1}L\textsubscript{2} or L\textsubscript{1}L\textsubscript{2}V pressure;

3) Dissolution of CO\textsubscript{2}, C\textsubscript{3}H\textsubscript{8} or $n$-C\textsubscript{4}H\textsubscript{10} in heavy oil at the L\textsubscript{1} or L\textsubscript{1}V equilibrium state contributes to an enhanced swelling factor, a reduced mixture viscosity and a reduced interfacial tension, which is fundamentally beneficial for enhancing heavy oil recovery;

4) The solubility of a gas in heavy oil depends proportionally on its nonvolatility. Therefore, C\textsubscript{3}H\textsubscript{8} and $n$-C\textsubscript{4}H\textsubscript{10} are potentially good solvent additives for the CO\textsubscript{2}-heavy oil system due to their high solubility in heavy oil and consequently desirable physical properties of the solvent-heavy oil mixture; and

5) Although the existing methods are suitable for estimating the apparent molecular diffusion coefficient of a gas mixture diffusing into heavy oil, they cannot be used to determine the individual molecular diffusion coefficient of each component in the solvent(s)-CO\textsubscript{2} mixture. Gas-phase compositional measurements may need to
be carried out before the diffusion test and after the diffusion test in order to determine the individual molecular diffusion coefficients of different gases in heavy oil.
CHAPTER 3 A MODIFIED ALPHA FUNCTION FOR PENG-ROBINSON EQUATION OF STATE TO IMPROVE VAPOUR PRESSURE PREDICTION OF NON-HYDROCARBON AND HYDROCARBON COMPOUNDS

3.1 Introduction

The cubic equation of state (CEOS)-based phase behaviour simulation of highly asymmetric systems plays a critical role in many enhanced oil recovery (EOR) processes, such as CO₂ injection (Kokal and Sayegh, 1989) and VAPEX processes (Upreti et al., 2007). These processes are closely associated with both the injected light compounds (e.g., CO₂ and C₃H₈) and light-to-heavy hydrocarbons. Although accurate prediction of phase behaviour of mixtures using EOS depends on the appropriately chosen binary interaction parameters and mixing rules, accurate representation of saturation conditions of pure substances by the alpha function in CEOS lays a sound foundation for successfully applying the EOS to mixtures.

The two-parameter CEOS has been widely used in the petroleum and chemical industries due to its simplicity and capability in predicting properties of pure substances and mixtures in both vapour and liquid phases. It has been well-accepted that the most popular two-parameter CEOS includes the PR EOS (Peng and Robinson, 1976) and the Soave-Redlich-Kwong equation of state (SRK EOS) (Soave, 1972). The attractive term associated with the alpha function in the CEOS plays an important role in accurately predicting the characteristics of a real pure substance deviated from its ideal behaviour. In general, an improved representation of the vapour pressures of pure substances leads to
an improved saturation pressure prediction for mixtures (Hernández-Garduza et al., 2002; Joshipura et al., 2009; Neau et al., 2009a). In the literature, numerous efforts have been made to modify the original alpha function for better phase behaviour simulation; however, most of the existing modified alpha functions are associated with non-hydrocarbon compounds and light hydrocarbons (Mathias, 1983; Mathias and Copeman, 1983; Stryjek and Vera, 1986; Melhem et al., 1989).

To modify the alpha function, the following three basic requirements should be satisfied: 1) the alpha function must be finite and positive at all temperatures; 2) alpha function equals unity at the critical point; and 3) the alpha function approaches a finite value as the temperature approaches infinity (Hernández-Garduza et al., 2002). In fact, the first two requirements can be easily satisfied for any alpha function. It is worthwhile noting that the traditional Soave-type alpha function fails to meet the third requirement since it does not demonstrate a limiting behaviour when the reduced temperature approaches infinity (Soave, 1972). However, as suggested by Neau et al. (2009a; b), the temperature point where the Soave alpha function begins to show upward trend is usually very high and beyond the interest of industrial applications. Thereafter, the third requirement is somewhat less restrictive.

The logarithm-type alpha function, which was proposed by Heyen (1981), and later modified by Treble and Bishnoi (1987), and Twu et al. (1991; 1995a; b), shows an asymptotic behaviour when the reduced temperature is approaching infinity. Twu’s alpha function employs a switching function which is defined by two sets of coefficients for the subcritical and supercritical conditions, respectively.
In this chapter, the functionality of two basic forms of the alpha function (i.e., the Soave-type alpha function and logarithm-type alpha function including the one recently modified by Gasem et al. (2001) for heavy hydrocarbons) in predicting the saturation properties of diverse pure substances was first examined. A new alpha function that combines the characteristics of both Soave-type and logarithm-type alpha functions is then developed, validated, and compared with the commonly used alpha functions. In addition, the acentric factor has been redefined at a reduced temperature of 0.6, rather than 0.7 as initially defined by Pitzer (1955) and Pitzer et al. (1955), and subsequently redefined as 0.5 by Twu et al. (1994), in an attempt to improve the saturation representation of both non-hydrocarbon and hydrocarbon compounds. The vapour pressure database in this study includes 59 chemical species from both light compounds, such as CO₂, CH₄ and C₃H₈, to heavy hydrocarbons up to n-tritetracontane (n-C₄₃H₈₈).

3.2 Mathematical Formulation

3.2.1. Alpha function

Due to its wide application in the petroleum and chemical industries, the PR EOS is chosen as the primary CEOS for this study. The same methodology discussed here will be also applicable to the SRK EOS. The PR EOS (Peng and Robinson, 1976) was originated from Redlich-Kwong EOS (1949) and SRK EOS (Soave, 1972) and can be expressed as follows,

\[
P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)}
\]  \[3-1\]

\[a = a_c \alpha(T_c, \omega)\]  \[3-2\]

44
where $\alpha(T_r, \omega)$ is the so-called alpha function which is dependent on both the reduced temperature $T_r$ and the acentric factor $\omega$, $P$ is the pressure, $T$ is the temperature, $V$ is the molar volume, $R$ is the universal gas constant, $P_c$ is the critical pressure, and $T_c$ is the critical temperature. Many modified versions of the alpha function have been made available in an attempt to enhance the vapour pressure prediction. A comprehensive review of the available alpha functions can be found elsewhere (Gasem et al., 2001).

In principle, the existing alpha functions can be divided into two categories, i.e., Soave-type alpha function and logarithm-type alpha function. The Soave-type alpha function is based on the observation that $\alpha$ varies with the reduced temperature in the following manner,

$$\alpha^{0.5} \propto \left(1 - T_r^{0.5}\right) \quad [3-5]$$

The Soave-type alpha function used in the PR EOS is given by,

$$\alpha = \left[1 + \left(0.37464 + 1.54226 \omega - 0.26992 \omega^2\right)(1 - T_r^{0.5})\right]^2 \quad [3-6]$$

A new form of the alpha function for $\omega > 0.49$ is later proposed by Robinson and Peng (1978),

$$\alpha = \left[1 + \left(0.3796 + 1.485 \omega - 0.1644 \omega^2 + 0.01667 \omega^3\right)(1 - T_r^{0.5})\right]^2 \quad [3-7]$$
As for the logarithm-type alpha function, variation of $\alpha$ with the reduced temperature can be expressed by,

$$\ln \alpha \propto (1 - T_r)$$  \hspace{1cm} [3-8]

The original logarithm-type alpha function was proposed by Heyen (1981) in the following form,

$$\alpha = \exp[k(1 - T_r^n)]$$  \hspace{1cm} [3-9]

and then was modified by Trebble and Bishnoi (1987) by removing the index, $n$ ,

$$\alpha = \exp[k(1 - T_r)]$$  \hspace{1cm} [3-10]

For both types of alpha functions, there exists an approximately linear relationship between $\alpha$ and the acentric factor, $\omega$. The $\alpha$ value for a substance at a subcritical temperature can be obtained by using a procedure that forces the fugacity of the gas phase to equate with that of liquid phase at the saturation pressure and temperature by using the CEOS (McCain, 1990). In order to explore the applicability of the Soave-type and logarithm-type alpha functions in representing vapour pressures of heavy hydrocarbons, the alpha values in the PR EOS for several heavy alkanes at different reduced temperatures are calculated and depicted in FIGUREs 3-1 and 3-2, respectively. It can be seen that both Soave-type and logarithm-type alpha functions are sufficiently accurate for representing the relation between $\alpha$ and the reduced temperature for heavy hydrocarbons up to $n$-tritetacontane ($n$-C$_{43}$H$_{88}$). This justifies the fact that either the Soave-type or logarithm-type relationship can be employed to accurately define the alpha function in the PR EOS.
FIGURE 3-1: Temperature dependence of the alpha function in the PR EOS for heavy normal alkanes expressed in Soave-type form (based on the experimental data (Mazee, 1948))
FIGURE 3-2: Temperature dependence of the alpha function in PR EOS for heavy normal alkanes expressed in logarithm-type form (based on the experimental data (Mazee, 1948))
In this chapter, a new alpha function has been developed by combining the advantages of both the Soave-type and logarithm-type alpha function with the following two possible methodologies. One is to sum the Soave-type alpha function and logarithm-type alpha function by using a weighting factor as shown below,

$$\alpha = w \exp\left[k_1 (1 - T_r)\right] + (1 - w)\left[1 + k_2 \left(1 - \sqrt{T_r}\right)\right]^2$$ \[3-11\]

where \(w\) is the weighting factor with values between 0 and 1. It can be found that the alpha defined by Equation [3-11] satisfies the first two aforementioned requirements; however, it can be easily derived that such type of alpha function does not show asymptotic behaviour when temperature approaches infinity. The alternative option would be to multiply the Soave-type with logarithm-type alpha function by using a weighting factor as a power index, i.e.,

$$\alpha = \left\{\exp[k'_1 (1 - T_r)]\right\}^w \left[1 + k_2 \left(1 - \sqrt{T_r}\right)\right]^{2(1-w)}$$ \[3-12\]

Obviously, Equation [3-12] can be reduced to Equation [3-6] with \(w\) equal to 0 and Equation [3-10] with \(w\) equal to 1, respectively. After carrying out some mathematical manipulations, Equation [3-12] can be simplified as,

$$\alpha = \exp\left\{k_1 (1 - T_r) + w \ln\left[1 + k_2 \left(1 - \sqrt{T_r}\right)\right]^{2(1-w)}\right\}$$ \[3-13\]

with

$$k_1 = k'_1 w = a_1 + a_2 \omega + a_3 \omega^2 + a_4 \omega^3$$ \[3-14a\]

$$k_2 = a_5 + a_6 \omega + a_7 \omega^2 + a_8 \omega^3$$ \[3-14b\]
and \( l \) is a constant that needs to be optimized. It can be shown that the new alpha function satisfies all the three basic requirements for a generalized alpha function, provided that the coefficient \( k_i > 0 \).

For the existing alpha functions, the numerical coefficients appearing in the \( \alpha \) expressions are determined by minimizing the deviation of the theoretically calculated and experimentally measured vapour pressures of a pure substance. Since Equations [3-6] and [3-7] are intrinsically developed on the basis of a limited number of substances including some light compounds and light-to-medium heavy hydrocarbons (Peng and Robinson, 1976; Robinson and Peng, 1978), extrapolation of these two equations to heavy hydrocarbons is expected to result in large deviations between the predicted vapour pressures and measured values. Gasem et al. (2001) modified the logarithm-type alpha function and obtained best reproduction of the vapour pressures of heavy hydrocarbons up to \( n \)-octacosane (\( n-C_{28}H_{58} \)) in comparison to the existing alpha functions.

Recently, based on the vapour pressure data of 237 hydrocarbons including heavy alkanes up to \( n \)-hexacosane (\( n-C_{26}H_{54} \)), Nji et al. (2009) modified the Soave-type alpha function for the PR EOS so that vapour pressures of heavy hydrocarbons can be more accurately predicted. Since the alpha functions developed by Gasem et al. (2001) and Nji et al. (2009) include heavy hydrocarbons in the database, these two alpha functions as well as the original Soave-type alpha function will be discussed in this chapter for the purpose of comparison. The experimentally measured vapour pressure data of heavy alkanes up to \( n \)-tritetracontane (\( n-C_{43}H_{88} \)) from Mazee et al. (1948) are included in this study (see TABLE 3-1). The formats of the evaluated alpha functions are summarized in TABLE 3-2.
**TABLE 3-1:** Vapour pressure database used in this study

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$T_r$</th>
<th>$P_{v}^{exp}$ (kPa)</th>
<th>NPTS*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>0.714-0.905</td>
<td>530.325-7368.95</td>
<td>55</td>
<td>Michels et al., 1950</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N₂</td>
<td>0.500-1.000</td>
<td>12.52-3400.2</td>
<td>67</td>
<td>Wagner, 1973</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>0.556-0.999</td>
<td>68.95-4857.8</td>
<td>57</td>
<td>Wagner, 1973</td>
</tr>
<tr>
<td>Neon</td>
<td>Ne</td>
<td>0.611-0.954</td>
<td>101.325-2026.5</td>
<td>5</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>0.422-1.000</td>
<td>0.6107-22106</td>
<td>78</td>
<td>Ambrose and Lawenson, 1972</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O₂</td>
<td>0.420-0.993</td>
<td>0.152-4844.8</td>
<td>22</td>
<td>Chung, 1997</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>0.691-0.996</td>
<td>558-10973.69</td>
<td>30</td>
<td>Baehr, 1976; Holcomb and Outcalt, 1999</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>HF</td>
<td>0.592-0.657</td>
<td>48.03-144.56</td>
<td>14</td>
<td>Sheft et al., 1973</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H₂S</td>
<td>0.496-0.589</td>
<td>17.399-141.655</td>
<td>8</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>0.609-0.976</td>
<td>101.325-3039.75</td>
<td>6</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>0.674-0.990</td>
<td>101.325-6079.5</td>
<td>9</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl₂</td>
<td>0.574-0.959</td>
<td>101.325-6079.5</td>
<td>9</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>SO₂</td>
<td>0.611-0.963</td>
<td>101.325-6079.5</td>
<td>9</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br₂</td>
<td>0.567-0.884</td>
<td>101.325-6079.5</td>
<td>9</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Krypton</td>
<td>Kr</td>
<td>0.578-0.987</td>
<td>101.325-5066.25</td>
<td>10</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td>SiCl₄</td>
<td>0.729-0.973</td>
<td>202.65-3039.75</td>
<td>5</td>
<td>Stull, 1947</td>
</tr>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>0.510-0.690</td>
<td>4.267-201.571</td>
<td>29</td>
<td>Ambrose et al., 1974</td>
</tr>
<tr>
<td>Ethyl fluoride</td>
<td>C₂H₅F</td>
<td>0.628-0.992</td>
<td>101.5-4713.9</td>
<td>110</td>
<td>Chen et al., 2005</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>C₂H₄O₂</td>
<td>0.513-0.700</td>
<td>2.891-201.718</td>
<td>27</td>
<td>Ambrose et al., 1977</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₄O</td>
<td>0.562-0.696</td>
<td>9.815-205.653</td>
<td>20</td>
<td>Ambrose and Sprake, 1970</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₆O</td>
<td>0.570-0.713</td>
<td>5.726-179.321</td>
<td>25</td>
<td>Ambrose and Sprake, 1970</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>C₅H₁₂O</td>
<td>0.744-0.874</td>
<td>226.8-1220</td>
<td>13</td>
<td>Ambrose et al., 1975</td>
</tr>
</tbody>
</table>
TABLE 3-1: Vapour pressure database used in this study (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>( T_r )</th>
<th>( P_{v}^{exp} ) (kPa)</th>
<th>NPTS*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octanol</td>
<td>( C_8H_{18}O )</td>
<td>0.770-0.849</td>
<td>234.6-649.9</td>
<td>10</td>
<td>Ambrose et al., 1975</td>
</tr>
<tr>
<td>Methane</td>
<td>( CH_4 )</td>
<td>0.476-1.000</td>
<td>11.698-4596.087</td>
<td>36</td>
<td>Kleinrahm and Wagner, 1986</td>
</tr>
<tr>
<td>Ethane</td>
<td>( C_2H_6 )</td>
<td>0.780-1.000</td>
<td>912.990-4863.500</td>
<td>18</td>
<td>Douslin and Harrison, 1973</td>
</tr>
<tr>
<td>Propane</td>
<td>( C_3H_8 )</td>
<td>0.698-1.000</td>
<td>291.79-4239.31</td>
<td>24</td>
<td>Thomast and Harrison, 1982</td>
</tr>
<tr>
<td>n-Butane</td>
<td>( n-C_4H_{10} )</td>
<td>0.753-0.995</td>
<td>456.65-3661.2</td>
<td>12</td>
<td>Kratzke, 1982</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>( i-C_4H_{10} )</td>
<td>0.681-0.844</td>
<td>183.194-1113.365</td>
<td>5</td>
<td>Martinez-Ortiz and Manley, 1978</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>( n-C_5H_{12} )</td>
<td>0.745-0.980</td>
<td>338.78-2912.7</td>
<td>14</td>
<td>Kratzke et al., 1985</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>( n-C_6H_{14} )</td>
<td>0.581-0.692</td>
<td>17.309-133.974</td>
<td>45</td>
<td>Bich et al., 1992</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>( n-C_7H_{16} )</td>
<td>0.687-0.889</td>
<td>99.663-1597.746</td>
<td>29</td>
<td>Weber, 2000</td>
</tr>
<tr>
<td>n-Octane</td>
<td>( n-C_8H_{18} )</td>
<td>0.632-0.691</td>
<td>29.037-86.150</td>
<td>15</td>
<td>Gregorowicz, 1987</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>( n-C_9H_{20} )</td>
<td>0.607-0.859</td>
<td>13.238-656.657</td>
<td>10</td>
<td>Carmichael, 1953</td>
</tr>
<tr>
<td>n-Decane</td>
<td>( n-C_{10}H_{22} )</td>
<td>0.528-0.961</td>
<td>0.8741-1395.0</td>
<td>16</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>( n-C_{12}H_{26} )</td>
<td>0.537-0.894</td>
<td>0.7338-671.13</td>
<td>13</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>( n-C_{14}H_{30} )</td>
<td>0.538-0.849</td>
<td>0.443-343.45</td>
<td>16</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>( n-C_{16}H_{34} )</td>
<td>0.544-0.807</td>
<td>0.318-163.53</td>
<td>20</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Octadecane</td>
<td>( n-C_{18}H_{38} )</td>
<td>0.553-0.707</td>
<td>0.2656-22.730</td>
<td>12</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Nonadecane</td>
<td>( n-C_{19}H_{40} )</td>
<td>0.560-0.779</td>
<td>0.2550-73.66</td>
<td>16</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Eicosane</td>
<td>( n-C_{20}H_{42} )</td>
<td>0.564-0.759</td>
<td>0.2440-48.08</td>
<td>32</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Docosane</td>
<td>( n-C_{22}H_{46} )</td>
<td>0.576-0.729</td>
<td>0.2432-20.720</td>
<td>12</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Tetracosane</td>
<td>( n-C_{24}H_{50} )</td>
<td>0.566-0.735</td>
<td>0.0901-17.460</td>
<td>13</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Octacosane</td>
<td>( n-C_{28}H_{58} )</td>
<td>0.586-0.713</td>
<td>0.0821-6.001</td>
<td>14</td>
<td>Morgan and Kobayashi, 1994</td>
</tr>
<tr>
<td>n-Triacontane</td>
<td>( n-C_{30}H_{62} )</td>
<td>0.621-0.650</td>
<td>0.4000-0.7761</td>
<td>7</td>
<td>Mazee, 1948</td>
</tr>
</tbody>
</table>
## TABLE 3-1: Vapour pressure database used in this study (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$T_r$ (°C)</th>
<th>$P_{exp}^{exp}$ (kPa)</th>
<th>NPTS*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-Hentriacontane</td>
<td>$n$-C$<em>{31}$H$</em>{64}$</td>
<td>0.610-0.653</td>
<td>0.4000-0.7160</td>
<td>7</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>$n$-Tetratriacontane</td>
<td>$n$-C$<em>{34}$H$</em>{70}$</td>
<td>0.623-0.649</td>
<td>0.4000-0.4187</td>
<td>7</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>$n$-Pentatriacontane</td>
<td>$n$-C$<em>{35}$H$</em>{72}$</td>
<td>0.637-0.658</td>
<td>0.4000-0.4931</td>
<td>7</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>$n$-Hexatriacontane</td>
<td>$n$-C$<em>{36}$H$</em>{74}$</td>
<td>0.631-0.656</td>
<td>0.4000-0.3451</td>
<td>7</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>$n$-Tritetracontane</td>
<td>$n$-C$<em>{43}$H$</em>{88}$</td>
<td>0.648-0.683</td>
<td>0.4000-0.5247</td>
<td>8</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>Benzene</td>
<td>C$_6$H$_6$</td>
<td>0.530-0.996</td>
<td>12.471-4772.600</td>
<td>33</td>
<td>Ambrose et al., 1970; Ambrose, 1990</td>
</tr>
<tr>
<td>Tetralin</td>
<td>C$<em>{10}$H$</em>{12}$</td>
<td>0.492-0.616</td>
<td>1.443-39.128</td>
<td>11</td>
<td>Mokbel et al., 1998</td>
</tr>
<tr>
<td>$n$-Butylbenzene</td>
<td>C$<em>{10}$H$</em>{14}$</td>
<td>0.505-0.633</td>
<td>1.249-37.027</td>
<td>10</td>
<td>Mokbel et al., 1998</td>
</tr>
<tr>
<td>Cyclohexylbenzene</td>
<td>C$<em>{10}$H$</em>{16}$</td>
<td>0.545-0.626</td>
<td>4.104-29.700</td>
<td>7</td>
<td>Mokbel et al., 1998</td>
</tr>
<tr>
<td>$n$-Octylbenzene</td>
<td>C$<em>{14}$H$</em>{22}$</td>
<td>0.555-0.637</td>
<td>1.513-14.226</td>
<td>7</td>
<td>Mokbel et al., 1998</td>
</tr>
<tr>
<td>$n$-Undecylbenzene</td>
<td>C$<em>{17}$H$</em>{28}$</td>
<td>0.578-0.610</td>
<td>1.369-3.726</td>
<td>4</td>
<td>Mokbel et al., 1998</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>C$<em>5$H$</em>{10}$</td>
<td>0.476-0.671</td>
<td>2.781-191.64</td>
<td>13</td>
<td>Mokbel et al., 1995</td>
</tr>
<tr>
<td>Trans-decahydronaphtalene</td>
<td>C$<em>{10}$H$</em>{18}$</td>
<td>0.474-0.601</td>
<td>1.329-38.41</td>
<td>10</td>
<td>Mokbel et al., 1995</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>C$<em>7$H$</em>{14}$</td>
<td>0.480-0.686</td>
<td>1.785-163.7</td>
<td>13</td>
<td>Mokbel et al., 1995</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>C$<em>8$H$</em>{16}$</td>
<td>0.571-0.722</td>
<td>19.920-270.111</td>
<td>15</td>
<td>Mokbel et al., 1995</td>
</tr>
</tbody>
</table>

Note:
* NPTS represents the number of experimental data points
TABLE 3-2: Alpha functions examined in this study

<table>
<thead>
<tr>
<th>Model No.</th>
<th>Functions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[ \alpha = \left[ 1 + \left( 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \right) \left( 1 - T_r^{0.5} \right) \right]^2 ]</td>
<td>Soave, 1972</td>
</tr>
<tr>
<td>2</td>
<td>[ \alpha = \left[ 1 + \left( 0.388187 + 1.56132 \omega - 0.29014 \omega^2 + 0.0617513 \omega^3 \right) \left( 1 - T_r^{0.5} \right) \right]^2 ]</td>
<td>Nji et al., 2009</td>
</tr>
<tr>
<td>3</td>
<td>[ \alpha = \exp \left[ (2 + 0.8367T_r) \left( 1 - T_r^{0.134 - 0.05068 \omega - 0.0675 \omega^2} \right) \right] ]</td>
<td>Gasem et al., 2001</td>
</tr>
<tr>
<td>4</td>
<td>[ \alpha = \exp \left{ k_1 (1 - T_r) + \ln \left[ 1 + k_2 \left( 1 - \sqrt{T_r} \right)^2 \right] \right} ]</td>
<td>This work</td>
</tr>
</tbody>
</table>
The alpha function in the PR EOS is also dependent on the acentric factor, which reflects the deviation of acentricity or non-sphericity of a compound molecule from that of a simple fluid, such as argon and xenon (Pitzer et al., 1955a). The acentric factor was originally introduced by Pitzer and co-workers (1955a, b) and defined as the following form in terms of the reduced vapour pressure at a reduced temperature of 0.7,

$$\omega = -\log(P_{r=0.7}) - 1$$  \[3-15\]

It has been found that, based on the above definition, the generalized correlation developed by Pitzer et al. (1955a) can be used to accurately predict the vapour pressures at reduced temperatures between 0.7 and 1.0 but less accurately represent those at reduced temperatures lower than 0.7 (Twu et al., 1994). In other words, the acentric factor defined at reduced temperature of 0.7 can accurately reflect the characteristics of a substance (e.g., carbon dioxide and light hydrocarbons) at a temperature close to 70-100% of its critical temperature. However, it is less accurate of representing the characteristics of a substance (e.g., heavy hydrocarbons) at a temperature usually much lower than 70% of its critical temperature encountered in the industrial applications. Thus, Twu et al. (1994) modified the definition of acentric factor at a reduced temperature of 0.5 other than 0.7 and achieved a better representation of vapour pressures of heavy hydrocarbons at low reduced temperatures.

Nji et al. (2009) developed an alpha function based on the acentric factor at a reduced temperature of 0.5 and improved vapour pressure predictions for heavy hydrocarbons. Nevertheless, it should be noted that using the acentric factor defined at a reduced temperature of 0.5 may result in a biased representation for non-hydrocarbon compounds since the vapour pressure database used by Nji et al. (2009) only contains
hydrocarbons. In this study, the Pitzer acentric factor is redefined at a reduced temperature of 0.6 so as to balance the characteristics of both light compounds and heavy hydrocarbons,

\[ \omega' = -\log(P_r)_{T_r=0.6} - 1 \] \hspace{1cm} [3-16]

Herein, it is assumed that the reduced vapour pressure for imaginary simple fluids at a reduced temperature of 0.6 is exactly equal to 0.1 so that the acentric factor for imaginary simple fluids becomes zero according to Equation [3-16].

3.2.2. Determination of the correlation coefficients

In this study, a total of 59 chemical species (including polar and non-polar non-hydrocarbons, light and heavy hydrocarbons) are included in the vapour pressure database. TABLE 3-1 presents the temperature range for each substance within which vapour pressure data are measured, while the critical properties used in this study are listed in TABLE 3-3. Note that the critical properties of some heavy hydrocarbons are estimated using the asymptotic behaviour model (Gao et al., 2001) whenever the experimental critical properties are not available from the literature.

The commonly used Wagner equation is used to smooth the vapour pressure data (Wagner, 1973). Then, the acentric factors defined at a reduced temperature of either 0.7 or 0.6 can be calculated using the regressed Wagner equations, as shown in TABLE 3-3. In particular, for normal alkanes, it is found that the acentric factor increases with carbon number of normal alkanes, as indicated by FIGURE 3-3. Quadratic polynomials are employed to describe the variation trend of acentric factor defined at \( T_r = 0.7 \) and 0.6 with carbon number. The regressed expressions for acentric factor defined at \( T_r = 0.7 \) and
**TABLE 3-3:** Critical properties and acentric factors of the substances used in this study

<table>
<thead>
<tr>
<th>Name</th>
<th>$P_c$ (kPa)</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
<th>$\omega^a$</th>
<th>$\omega'^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>7377.5</td>
<td>304.14</td>
<td>Shaver et al., 1991</td>
<td>0.2238</td>
<td>0.9276</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3400.2</td>
<td>126.2</td>
<td>Shaver et al., 1991</td>
<td>0.0371</td>
<td>0.6119</td>
</tr>
<tr>
<td>Argon</td>
<td>4897.9</td>
<td>150.86</td>
<td>Shaver et al., 1991</td>
<td>-0.0031</td>
<td>0.5422</td>
</tr>
<tr>
<td>Neon</td>
<td>2653</td>
<td>44.4</td>
<td>Green and Perry, 2008</td>
<td>0.3451</td>
<td>1.1142</td>
</tr>
<tr>
<td>Water</td>
<td>22055</td>
<td>647.13</td>
<td>Shaver et al., 1991</td>
<td>0.3451</td>
<td>1.1142</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5042.9</td>
<td>154.581</td>
<td>Shaver et al., 1991</td>
<td>0.0222</td>
<td>0.5852</td>
</tr>
<tr>
<td>Ammonia</td>
<td>11304</td>
<td>405.4</td>
<td>Shaver et al., 1991</td>
<td>0.2519</td>
<td>0.9630</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>6480</td>
<td>461.15</td>
<td>Shaver et al., 1991</td>
<td>0.3798</td>
<td>1.0701</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>8970</td>
<td>373.3</td>
<td>Green and Perry, 2008</td>
<td>0.2137</td>
<td>0.7341</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>3498.75</td>
<td>134.45</td>
<td>Green and Perry, 2008</td>
<td>0.0916</td>
<td>0.5880</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>6480</td>
<td>180.15</td>
<td>Green and Perry, 2008</td>
<td>0.5885</td>
<td>1.4627</td>
</tr>
<tr>
<td>Chlorine</td>
<td>7710</td>
<td>417.15</td>
<td>Green and Perry, 2008</td>
<td>0.0735</td>
<td>0.6823</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>7884</td>
<td>430.75</td>
<td>Green and Perry, 2008</td>
<td>0.2441</td>
<td>0.9852</td>
</tr>
<tr>
<td>Bromine</td>
<td>10300</td>
<td>584.15</td>
<td>Green and Perry, 2008</td>
<td>0.0465</td>
<td>0.7217</td>
</tr>
<tr>
<td>Krypton</td>
<td>5520.19</td>
<td>209.46</td>
<td>Green and Perry, 2008</td>
<td>-0.0589</td>
<td>0.5739</td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td>3720</td>
<td>259</td>
<td>Green and Perry, 2008</td>
<td>0.4768</td>
<td>1.4415</td>
</tr>
<tr>
<td>Acetone</td>
<td>4700</td>
<td>508.1</td>
<td>Shaver et al., 1991</td>
<td>0.3074</td>
<td>1.0613</td>
</tr>
<tr>
<td>Ethyl fluoride</td>
<td>5027.75</td>
<td>375.31</td>
<td>Chen et al., 2005</td>
<td>0.2170</td>
<td>0.9159</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>5786</td>
<td>592.71</td>
<td>Shaver et al., 1991</td>
<td>0.4598</td>
<td>1.2803</td>
</tr>
<tr>
<td>Methanol</td>
<td>8097.1</td>
<td>512.64</td>
<td>Shaver et al., 1991</td>
<td>0.5652</td>
<td>1.4737</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6148.4</td>
<td>513.92</td>
<td>Shaver et al., 1991</td>
<td>0.6451</td>
<td>1.6455</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>3897</td>
<td>588.1</td>
<td>Shaver et al., 1991</td>
<td>0.5785</td>
<td>1.6294</td>
</tr>
</tbody>
</table>
TABLE 3-3: Critical properties and acentric factors of the substances used in this study (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>$P_c$ (kPa)</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
<th>$\omega^a$</th>
<th>$\omega'^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octanol</td>
<td>2783</td>
<td>652.3</td>
<td>Shaver et al., 1991</td>
<td>0.5801</td>
<td>1.6031</td>
</tr>
<tr>
<td>Methane</td>
<td>4599.2</td>
<td>190.564</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.0103</td>
<td>0.5640</td>
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<tr>
<td>Ethane</td>
<td>4871.8</td>
<td>305.322</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.0989</td>
<td>0.7090</td>
</tr>
<tr>
<td>Propane</td>
<td>4246.2</td>
<td>369.825</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.1520</td>
<td>0.8007</td>
</tr>
<tr>
<td>$n$-Butane</td>
<td>3786.1</td>
<td>425.12</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.1978</td>
<td>0.8749</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>3640</td>
<td>407.8</td>
<td>Martinez-Ortlz and Manley, 1978</td>
<td>0.1852</td>
<td>0.8592</td>
</tr>
<tr>
<td>$n$-Pentane</td>
<td>3366.5</td>
<td>469.7</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.2501</td>
<td>0.9644</td>
</tr>
<tr>
<td>$n$-Hexane</td>
<td>3018.1</td>
<td>507.49</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.2988</td>
<td>1.0585</td>
</tr>
<tr>
<td>$n$-Heptane</td>
<td>2727</td>
<td>540.13</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.3486</td>
<td>1.1384</td>
</tr>
<tr>
<td>$n$-Octane</td>
<td>2486</td>
<td>568.88</td>
<td>Lemmon and Goodwin, 2000</td>
<td>0.3971</td>
<td>1.2251</td>
</tr>
<tr>
<td>$n$-Nonane</td>
<td>2290</td>
<td>594.6</td>
<td>Nikitin et al., 1997</td>
<td>0.4442</td>
<td>1.3093</td>
</tr>
<tr>
<td>$n$-Decane</td>
<td>2110</td>
<td>617.7</td>
<td>Nikitin et al., 1997</td>
<td>0.5381</td>
<td>1.4549</td>
</tr>
<tr>
<td>$n$-Dodecane</td>
<td>1820</td>
<td>658.32</td>
<td>Nikitin et al., 1997</td>
<td>0.5757</td>
<td>1.5381</td>
</tr>
<tr>
<td>$n$-Tetradecane</td>
<td>1570</td>
<td>693</td>
<td>Nikitin et al., 1997</td>
<td>0.6442</td>
<td>1.6671</td>
</tr>
<tr>
<td>$n$-Hexadecane</td>
<td>1400</td>
<td>723</td>
<td>Nikitin et al., 1997</td>
<td>0.7167</td>
<td>1.7962</td>
</tr>
<tr>
<td>$n$-Octadecane</td>
<td>1290</td>
<td>747</td>
<td>Nikitin et al., 1997</td>
<td>0.8160</td>
<td>1.9565</td>
</tr>
<tr>
<td>$n$-Nonadecane</td>
<td>1160</td>
<td>755</td>
<td>Nikitin et al., 1997</td>
<td>0.8624</td>
<td>2.0343</td>
</tr>
<tr>
<td>$n$-Eicosane</td>
<td>1080</td>
<td>768</td>
<td>Nikitin et al., 1997</td>
<td>0.88665$^b$</td>
<td>2.0686</td>
</tr>
<tr>
<td>$n$-Docosane</td>
<td>991</td>
<td>786</td>
<td>Nikitin et al., 1997</td>
<td>0.9579</td>
<td>2.2213</td>
</tr>
<tr>
<td>$n$-Tetracosane</td>
<td>871</td>
<td>800</td>
<td>Nikitin et al., 1997</td>
<td>1.0509</td>
<td>2.3841</td>
</tr>
<tr>
<td>$n$-Octacosane</td>
<td>744</td>
<td>824</td>
<td>Nikitin et al., 1997</td>
<td>1.1702</td>
<td>2.60767$^c$</td>
</tr>
<tr>
<td>$n$-Triacontane</td>
<td>636</td>
<td>843</td>
<td>Nikitin et al., 1997</td>
<td>1.2188</td>
<td>2.6921</td>
</tr>
</tbody>
</table>
TABLE 3-3: Critical properties and acentric factors of the substances used in this study (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>$P_c$ (kPa)</th>
<th>$T_c$ (K)</th>
<th>Reference</th>
<th>$\omega^a$</th>
<th>$\omega'^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$-Hentriacontane</td>
<td>607.37</td>
<td>847.58</td>
<td>Gao et al., 2001</td>
<td>1.2654</td>
<td>2.7815</td>
</tr>
<tr>
<td>$n$-Tetracontane</td>
<td>526.64</td>
<td>862.41</td>
<td>Gao et al., 2001</td>
<td>1.3447</td>
<td>2.9135</td>
</tr>
<tr>
<td>$n$-Pentatriacontane</td>
<td>502.8</td>
<td>866.88</td>
<td>Gao et al., 2001</td>
<td>1.4149</td>
<td>2.9391</td>
</tr>
<tr>
<td>$n$-Hexatriacontane</td>
<td>472</td>
<td>872</td>
<td>Nikitin et al., 1997</td>
<td>1.4243</td>
<td>2.9937</td>
</tr>
<tr>
<td>$n$-Tritetracontane</td>
<td>353.66</td>
<td>896.03</td>
<td>Gao et al., 2001</td>
<td>1.5439</td>
<td>3.3847</td>
</tr>
<tr>
<td>Benzene</td>
<td>4889.8</td>
<td>562.161</td>
<td>Shaver et al., 1991</td>
<td>0.2084</td>
<td>0.9088</td>
</tr>
<tr>
<td>Tetralin</td>
<td>4889.8</td>
<td>562.161</td>
<td>Mokbel et al., 1998</td>
<td>0.3220</td>
<td>1.1156</td>
</tr>
<tr>
<td>$n$-Butylbenzene</td>
<td>2890</td>
<td>660.5</td>
<td>Mokbel et al., 1998</td>
<td>0.3517</td>
<td>1.2085</td>
</tr>
<tr>
<td>Cyclohexylbenzene</td>
<td>2890</td>
<td>739.6</td>
<td>Mokbel et al., 1998</td>
<td>0.4203</td>
<td>1.2280</td>
</tr>
<tr>
<td>$n$-Octylbenzene</td>
<td>1980</td>
<td>726.7</td>
<td>Mokbel et al., 1998</td>
<td>0.5943</td>
<td>1.5357</td>
</tr>
<tr>
<td>$n$-Undecylbenzene</td>
<td>1610</td>
<td>765.5</td>
<td>Mokbel et al., 1998</td>
<td>0.7156</td>
<td>1.7677</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>4510</td>
<td>511.7</td>
<td>Lide, 2009</td>
<td>0.1972</td>
<td>0.8792</td>
</tr>
<tr>
<td>Trans-decahydronaphtalene</td>
<td>3200</td>
<td>703.6</td>
<td>Lide, 2009</td>
<td>0.2089</td>
<td>0.9291</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>3480</td>
<td>572.1</td>
<td>Lide, 2009</td>
<td>0.2407</td>
<td>0.9533</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>3560</td>
<td>647.2</td>
<td>Lide, 2009</td>
<td>0.2522</td>
<td>0.9863</td>
</tr>
</tbody>
</table>

Note:

$^a$ Calculated based on the experimental data and Wagner equation

$^b$ Smoothed value using Equation [3-17]

$^c$ Smoothed value using Equation [3-18]
FIGURE 3-3: Dependence of acentric factor on carbon number of normal alkanes
0.6 are respectively provided as follows,

\[ \omega = 0.0520C_n - 0.0004C_n^2 \]  \hspace{1cm} [3-17]

and

\[ \omega' = 0.5268 + 0.0907C_n - 0.0006C_n^2 \]  \hspace{1cm} [3-18]

The above two equations are regressed with a confidence interval of 95%. The standard errors for the fitted coefficients are shown in TABLE 3-4. The purpose of the regression is to obtain the coefficients that appear in the new alpha function expressed by Equation [3-13] based on the vapour pressure database considered. Such regression can be achieved by minimizing the objective function defined as follows,

\[ \text{RMSRE} = \sqrt{\frac{1}{NPTS} \sum_{i=1}^{NPTS} \left( \frac{P_{\text{cal},i} - P_{\text{exp},i}}{P_{\text{exp},i}} \right)^2} \]  \hspace{1cm} [3-19]

All the regressions have been conducted with a confidence interval of 95%. To ensure that the new alpha function demonstrates the asymptotic behaviour when the reduced temperature is approaching infinity, the following constraint is applied.

\[ \min \{ k_i = a_1 + a_2\omega_i + a_3\omega_i^2 + a_4\omega_i^3, i = 1,2,3,\ldots,m \} > 0 \]  \hspace{1cm} [3-20]

where \( m \) is the total number of compound species considered in this study. This constraint ensures the coefficient \( k_i > 0 \).

The alpha function with an acentric factor defined at reduced temperature of 0.7 is obtained as follows,

\[ \alpha = \exp \left\{ \left( 0.13280 - 0.05052\omega + 0.25948\omega^2 \right)(1 - T_r) + 0.81769\ln \left[ 1 + \left( 0.31355 + 1.86745\omega - 0.52604\omega^2 \right)(1 - \sqrt{T_r}) \right]^2 \right\} \]  \hspace{1cm} [3-21]
TABLE 3-4: Standard errors of the fitted coefficients in Equations [3-17] and [3-18]

<table>
<thead>
<tr>
<th>Equation [3-17]</th>
<th></th>
<th>Equation [3-18]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficient</td>
<td>Standard error</td>
<td>Coefficient</td>
<td>Standard error</td>
</tr>
<tr>
<td>0.05200</td>
<td>0.00070</td>
<td>0.52680</td>
<td>0.01880</td>
</tr>
<tr>
<td>-0.00040</td>
<td>0.00002</td>
<td>0.09070</td>
<td>0.00230</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-0.00060</td>
<td>0.00005</td>
</tr>
</tbody>
</table>
Under supercritical states, the Soave-type function, even with its abnormal minimum at a very high temperature, must be preferred to the logarithm types which usually present inconsistent variations of the alpha function with respect to temperature (Neau et al., 2009a; b). Therefore, the proposed Equation [3-21] is recommended for subcritical region ($T_r \leq 1$) and the following Soave-type alpha function instead of Equation [3-21] should be used under supercritical states ($T_r > 1$),

$$\alpha = \left[ 1 + (0.38856 + 1.40137\omega - 0.05387\omega^2 - 0.01824\omega^3)(1 - T_r^{0.5}) \right]^2 \quad [3-22]$$

The alpha function with an acentric factor defined at reduced temperature of 0.6 is determined as,

$$\alpha = \exp \left\{ \left( \frac{0.34580 - 0.59700\omega' + 0.27040\omega'\omega^2}{0.92030\ln \left[ 1 + \left( -0.53261 + 1.75415\omega' - 0.40127\omega'\omega^2 \right) \left( 1 - \sqrt{T_r} \right)^2 \right] } \right) \right\} \quad [3-23]$$

Similarly, Equation [3-23] is recommended for subcritical region ($T_r \leq 1$) and the following Soave-type alpha function instead of Equation [3-23] should be used for supercritical conditions ($T_r > 1$),

$$\alpha = \left[ 1 + \left( -0.12401 + 0.96953\omega' - 0.08591\omega'\omega^2 + 0.00642\omega^3 \right) \left( 1 - T_r^{0.5} \right) \right]^2 \quad [3-24]$$

The regressed coefficients in Equation [3-13] for acentric factors defined at $T_r = 0.7$ and 0.6 are specified in alpha functions [3-21] and [3-23], respectively. For convenience, the alpha functions expressed by Equations [3-21] and [3-23] are referred to as alpha functions #4-1 and 4-2. It can be found that the $k_i$ terms in the alpha functions #4-1 and 4-2 do not show a negative value even at a large and positive acentric factor. TABLE 3-5 lists the standard errors of the fitted coefficients appearing in alpha functions #4-1 and 4-
**TABLE 3-5:** Standard errors of the fitted coefficients in alpha functions #4-1 and 4-2

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Alpha function #4-1</th>
<th>Alpha function #4-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value</td>
<td>Standard error</td>
</tr>
<tr>
<td>$a_1$</td>
<td>0.13280</td>
<td>0.02954</td>
</tr>
<tr>
<td>$a_2$</td>
<td>-0.05052</td>
<td>0.00963</td>
</tr>
<tr>
<td>$a_3$</td>
<td>0.25948</td>
<td>0.03896</td>
</tr>
<tr>
<td>$a_5$</td>
<td>0.31355</td>
<td>0.07627</td>
</tr>
<tr>
<td>$a_6$</td>
<td>1.86745</td>
<td>0.10264</td>
</tr>
<tr>
<td>$a_7$</td>
<td>-0.52604</td>
<td>0.03418</td>
</tr>
<tr>
<td>$l$</td>
<td>0.81769</td>
<td>0.09159</td>
</tr>
</tbody>
</table>
2 with a regression confidence interval of 95%. For a given chemical species, alpha function #4-2 is decreased with an increase in reduced temperature. As shown in FIGURE 3-4, it can be observed that the alpha function developed by this study shows a monotonously decreasing dependence on the reduced temperature that is below 4 for carbon dioxide.

It is worthwhile noting that the recommended Soave-type alpha functions Equation [3-22] and Equation [3-24] for supercritical region are applicable for low-to-medium supercritical temperatures. In this case, the alpha functions will show an upward trend at a high supercritical temperature (about 3 to 4 times critical temperature), though such a high temperature is seldom encountered in petroleum and chemical applications.

3.2.3. Enthalpy of vaporization

The newly proposed alpha function, i.e., Equation [3-23], is used to calculate other thermodynamics properties in order to further validate its applicability. Due to the availability of vaporization enthalpy data for heavy hydrocarbons, vaporization enthalpy is chosen as the thermodynamic property for the purpose of validation. The fundamental enthalpy departure equation on a molar scale is provided as follows (Sandler, 1999),

\[
H(T, P) - H^G(T, P) = RT(Z - 1) + \int_{V=V(T, P)}^{V=\infty} \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \quad [3-25]
\]

More specific expression can be obtained using PR EOS as follows,

\[
H(T, P) - H^G(T, P) = RT(Z - 1) + \frac{T \left( \frac{da}{dT} \right) - a}{2\sqrt{2}b} \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \quad [3-26]
\]
FIGURE 3-4: Variation of alpha function #4-2 with reduced temperature for CO₂
Thus, the enthalpy of vaporization at saturation temperature can be readily expressed by,

$$\Delta_f^e H(T) = RT(Z_v - Z_l) + \frac{T\left(\frac{da}{dT}\right)}{2\sqrt{2b}} - a \left\{ \ln \left[ \frac{Z_v + (1 + \sqrt{2})B}{Z_v + (1 - \sqrt{2})B} \right] - \ln \left[ \frac{Z_l + (1 + \sqrt{2})B}{Z_l + (1 - \sqrt{2})B} \right] \right\}$$

[3-27]

where

$$B = \frac{bP}{RT}$$

[3-28]

and for the newly proposed alpha function,

$$\frac{d\alpha}{dt} = \left\{ -\frac{k_1}{T_c} - \frac{lk_2}{T_c\sqrt{T_r} \left[ 1 + k_2 \left( 1 - \sqrt{T_r} \right) \right]} \right\} \exp\left\{ k_1(1 - T_r) + \ln\left[ 1 + k_2 \left( 1 - \sqrt{T_r} \right) \right]^2 \right\}$$

[3-29]

TABLE 3-6 lists the vaporization enthalpy data of non-hydrocarbon compounds, light hydrocarbons and heavy hydrocarbons, which are found from the literature.

3.3 Results and Discussion

3.3.1. Vapour pressure

The predicted vapour pressures based on the aforementioned alpha functions are presented in TABLE 3-7 in terms of the percentage absolute average deviation (%AAD), the percentage bias (%BIAS), and the percentage maximum absolute deviation (%MAD). Alpha functions #1, 2, 3 and 4-1 shown in TABLE 3-7 are based on an acentric factor which is defined at $T_r = 0.7$, while alpha function #4-2 is based on an acentric factor that is defined at $T_r = 0.6$. It should be noted that the overall %AAD data for various alpha
<table>
<thead>
<tr>
<th>Name</th>
<th>( T ) (K)</th>
<th>( \Delta_f^\circ H(T) ) (kJ/mol)</th>
<th>NPTS</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>244.26-303.71</td>
<td>2.20-12.89</td>
<td>56</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>63.15-110.00</td>
<td>3.76-6.03</td>
<td>7</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Argon</td>
<td>83.81-150.00</td>
<td>1.17-6.54</td>
<td>8</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Water</td>
<td>273.15-643.15</td>
<td>16.07-45.01</td>
<td>28</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Benzene</td>
<td>295.00-460.00</td>
<td>23.19-33.40</td>
<td>34</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Oxygen</td>
<td>54.36-150.00</td>
<td>2.54-7.77</td>
<td>11</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Acetone</td>
<td>260.00-350.00</td>
<td>27.78-33.18</td>
<td>31</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Methanol</td>
<td>300.00-470.00</td>
<td>29.7-39.29</td>
<td>18</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Ethanol</td>
<td>300.00-460.00</td>
<td>33.82-44.48</td>
<td>17</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Methane</td>
<td>90.69-190.00</td>
<td>1.29-8.70</td>
<td>11</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Ethane</td>
<td>90.37-300.00</td>
<td>4.49-17.84</td>
<td>12</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>Propane</td>
<td>85.53-360.00</td>
<td>6.78-24.76</td>
<td>15</td>
<td>Lide, 2009</td>
</tr>
<tr>
<td>( n )-Pentane</td>
<td>298.15</td>
<td>26.4</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Hexane</td>
<td>298.15</td>
<td>31.5</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Heptane</td>
<td>298.15</td>
<td>36.6</td>
<td>1</td>
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</tr>
<tr>
<td>( n )-Octane</td>
<td>298.15</td>
<td>41.6</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Nonane</td>
<td>298.15</td>
<td>46.6</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Decane</td>
<td>298.15</td>
<td>51.4</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Undecane</td>
<td>298.15</td>
<td>56.6</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Dodecane</td>
<td>298.15</td>
<td>61.5</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Tridecane</td>
<td>298.15</td>
<td>66.7</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>( n )-Tetradecane</td>
<td>298.15</td>
<td>71.7</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>Name</td>
<td>T (K)</td>
<td>$\Delta_f^o H (T)$ (kJ/mol)</td>
<td>NPTS</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
<td>-----------------------------</td>
<td>------</td>
<td>----------------------</td>
</tr>
<tr>
<td>n-Pentadecane</td>
<td>298.15</td>
<td>76.8</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>298.15</td>
<td>81.4</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>n-Heptadecane</td>
<td>298.15</td>
<td>86.5</td>
<td>1</td>
<td>Chickos and Wilson, 1997</td>
</tr>
<tr>
<td>n-Eicosane</td>
<td>440.00</td>
<td>80.78</td>
<td>1</td>
<td>Chirico et al., 1989</td>
</tr>
<tr>
<td>n-Tetracosane</td>
<td>481.75</td>
<td>90.16</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Octacosane</td>
<td>515.15</td>
<td>93.72</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Triacontane</td>
<td>531.65</td>
<td>99.99</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Hentriacontane</td>
<td>539.35</td>
<td>105.00</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Tetratriacontane</td>
<td>558.55</td>
<td>107.90</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Pentatriacontane</td>
<td>565.45</td>
<td>111.50</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Hexatriacontane</td>
<td>571.55</td>
<td>114.80</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
<tr>
<td>n-Tritetracontane</td>
<td>605.15</td>
<td>131.40</td>
<td>1</td>
<td>Mazee, 1948</td>
</tr>
</tbody>
</table>
### TABLE 3-7: The predicted vapour pressures by using PR EOS with different alpha functions

<table>
<thead>
<tr>
<th>Name</th>
<th>%AAD of each model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.27</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.75</td>
</tr>
<tr>
<td>Argon</td>
<td>0.87</td>
</tr>
<tr>
<td>Neon</td>
<td>5.86</td>
</tr>
<tr>
<td>Water</td>
<td>4.65</td>
</tr>
<tr>
<td>Oxygen</td>
<td>2.05</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.34</td>
</tr>
<tr>
<td>Hydrogen fluoride</td>
<td>18.10</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>42.89</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>7.66</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>4.79</td>
</tr>
<tr>
<td>Chlorine</td>
<td>2.16</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>2.12</td>
</tr>
<tr>
<td>Bromine</td>
<td>17.39</td>
</tr>
<tr>
<td>Krypton</td>
<td>14.87</td>
</tr>
<tr>
<td>Silicon tetrachloride</td>
<td>3.42</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.52</td>
</tr>
<tr>
<td>Ethyl fluoride</td>
<td>0.54</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>10.53</td>
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<tr>
<td>Methanol</td>
<td>3.90</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.24</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>3.76</td>
</tr>
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</table>
### TABLE 3-7: The predicted vapour pressures by using PR EOS with different alpha functions (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>%AAD of each model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>1.67</td>
</tr>
<tr>
<td>Methane</td>
<td>0.67</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.34</td>
</tr>
<tr>
<td>Propane</td>
<td>0.26</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.36</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>0.42</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.25</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.70</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.25</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.52</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0.80</td>
</tr>
<tr>
<td>n-Decane</td>
<td>3.84</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>3.19</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>0.32</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>7.63</td>
</tr>
<tr>
<td>n-Octadecane</td>
<td>11.28</td>
</tr>
<tr>
<td>n-Nonadecane</td>
<td>10.82</td>
</tr>
<tr>
<td>n-Eicosane</td>
<td>14.36</td>
</tr>
<tr>
<td>n-Docosane</td>
<td>19.02</td>
</tr>
</tbody>
</table>
TABLE 3-7: The predicted vapour pressures by using PR EOS with different alpha functions (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>%AAD for each model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>n-Tetracosane</td>
<td>26.00</td>
</tr>
<tr>
<td>n-Octacosane</td>
<td>38.01</td>
</tr>
<tr>
<td>n-Triacontane</td>
<td>53.47</td>
</tr>
<tr>
<td>n-Hentriacontane</td>
<td>61.44</td>
</tr>
<tr>
<td>n-Tetracontane</td>
<td>69.69</td>
</tr>
<tr>
<td>n-Pentatriacontane</td>
<td>60.86</td>
</tr>
<tr>
<td>n-Hexatriacontane</td>
<td>69.93</td>
</tr>
<tr>
<td>n-Tritetracontane</td>
<td>98.70</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.02</td>
</tr>
<tr>
<td>Tetralin</td>
<td>9.85</td>
</tr>
<tr>
<td>n-Butylbenzene</td>
<td>21.62</td>
</tr>
<tr>
<td>Cyclohexylbenzene</td>
<td>7.06</td>
</tr>
<tr>
<td>n-Octylbenzene</td>
<td>2.69</td>
</tr>
<tr>
<td>n-Undecylbenzene</td>
<td>5.57</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>2.15</td>
</tr>
<tr>
<td>Trans-decahydronaphthalene</td>
<td>22.08</td>
</tr>
<tr>
<td>Methylene</td>
<td>1.65</td>
</tr>
<tr>
<td>Cetyl</td>
<td>1.62</td>
</tr>
<tr>
<td>Overall %AAD</td>
<td>7.10</td>
</tr>
<tr>
<td>%BIAS</td>
<td>4.10</td>
</tr>
<tr>
<td>%MAD</td>
<td>125.95</td>
</tr>
</tbody>
</table>
functions listed in TABLE 3-7 are calculated by averaging all the 1165 other than 59 %AAD data points for the 59 compounds. As can be seen from TABLE 3-7, the original form of the Soave-type function used in PR EOS results in the largest error for predicting vapour pressures for heavy hydrocarbons with %AAD increasing as a function of carbon number. This is mainly attributed to the fact that the original alpha function in PR-EOS is developed on the basis of vapour pressure of light hydrocarbons.

Both alpha function #2 and alpha function #3 demonstrate better prediction of vapour pressure for heavy hydrocarbons compared to the original Soave-type alpha function #1. It is worthwhile noting that alpha function #2 produces a second largest %AAD among all the examined alpha functions except for the original Soave-type alpha function #1. This can be ascribed to the fact that the vapour pressure data used to develop alpha function #2 is solely from hydrocarbons. In addition, the newly developed alpha functions #4-1 and 4-2 that combines the Soave-type form and logarithm-type form outperforms the Soave-type alpha functions #1 and 2 as well as the logarithm-type alpha function #3 since a better prediction in terms of %AAD between the experimentally measured and theoretically calculated vapour pressures has been obtained with the newly developed alpha function.

It is also interesting to find that, compared to the acentric factor defined at a reduced temperature of 0.7, this parameter defined at a reduced temperature of 0.6 enables alpha function #4-2 to provide a much better prediction of vapour pressures. For example, the overall %AAD and %MAD by using alpha function #4-2 with an acentric factor defined at $T_r = 0.6$ is reduced to 1.90% and 21.22%, compared to 2.87% and 40.56% resulting from alpha function #4-1 with an acentric factor defined at $T_r = 0.7$. In particular, a much
better prediction of vapour pressures of the polar compounds (e.g., hydrogen fluoride, hydrogen sulphide and acetic acid) and aromatic compounds (e.g., \( n \)-butylbenzene and trans-decahydronaphtalene) has been also observed by using the alpha function defined at \( T_r = 0.6 \) other than \( T_r = 0.7 \). This means that the acentric factor defined at \( T_r = 0.6 \) outperforms the acentric factor defined at \( T_r = 0.7 \) in reproducing vapour pressures of non-hydrocarbon compounds, light hydrocarbons and heavy hydrocarbons. Overall, TABLE 3-7 demonstrates that the alpha function #4-2 developed in this study provides the best vapour pressure prediction for all the examined chemical compounds.

FIGURE 3-5 illustrates %AAD variation of PR EOS prediction of normal-alkane vapour pressure against carbon number by incorporating different alpha functions. In general, the original PR EOS is found to be accurate in predicting the vapour pressure of normal alkanes with carbon number less than ten. Unfortunately, the average absolute deviation of vapour pressures between the experimental measurement and theoretical prediction using the original PR EOS increases drastically for normal alkanes with carbon number of ten and higher. This is attributed to the fact that the original alpha function in PR EOS is obtained mainly on the basis of vapour pressure data of light hydrocarbons. The other three alpha functions (#2, 3 and 4-2) show improved predictions of vapour pressure of heavier alkanes since vapour pressure data of heavy alkanes are included in the database with which the three alpha functions are developed. More accurate prediction of the vapour pressures of heavier alkanes can be obtained by using the newly developed alpha function #4-2 in comparison to the other alpha functions evaluated.
FIGURE 3-5: Overall %AAD of the predicted vapour pressures of normal alkanes using different alpha function models
3.3.2. Enthalpy of vaporization

In order to examine the capability of the newly proposed alpha function in representing other thermodynamic properties, alpha functions #1, 2, 3, and 4-2 are incorporated into the PR EOS to predict the vaporization enthalpy of the compounds as provided in TABLE 3-8. As can be seen from TABLE 3-8, the overall accuracy of the predicted vaporization enthalpy is slightly lower than that of the predicted vapour pressure for each compound. Alpha function #1 is found to yield the largest error in predicting the vaporization enthalpy, especially for the heavy alkanes, while the other three alpha functions demonstrate similar predictive accuracy. Among the four alpha functions examined by this study, the alpha function proposed in this study provides the most accurate prediction of vaporization enthalpy of all the compounds considered in terms of %AAD. This means that the proposed alpha function outperforms either the logarithm-type or Soave-type alpha functions with respect to the predicted vapour pressure and vaporization enthalpy.

3.4 Summary

A new alpha function for the PR EOS is developed to more accurately predict vapour pressure for non-hydrocarbons and hydrocarbon compounds, while the acentric factor is redefined at a reduced temperature of 0.6 and incorporated into the newly developed alpha function. Compared to the other existing alpha functions evaluated, the newly developed alpha function can be used to more accurately predict the vapour pressure for polar or non-polar non-hydrocarbon substances, light hydrocarbons and heavy
**TABLE 3-8:** The predicted vaporization enthalpy using PR EOS with different alpha functions

<table>
<thead>
<tr>
<th>Name</th>
<th>%AAD for each model</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>5.21 5.17 5.32 5.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.85 0.58 0.32 0.74</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argon</td>
<td>3.24 3.09 3.21 3.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>5.37 4.77 5.91 4.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.63 1.78 1.18 1.73</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.97 1.57 1.82 1.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>2.01 1.28 2.70 1.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>8.25 8.19 8.31 7.82</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>10.96 10.48 9.87 10.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>3.83 4.18 4.44 3.76</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>2.36 2.35 2.33 2.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>2.46 2.63 1.53 2.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.14 0.83 0.15 0.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Hexane</td>
<td>0.94 1.72 0.22 0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1.81 2.60 0.67 2.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Octane</td>
<td>2.47 3.19 0.91 1.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Nonane</td>
<td>3.11 3.70 1.16 3.14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Decane</td>
<td>0.94 0.75 3.51 0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Undecane</td>
<td>4.25 4.45 1.62 4.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>4.95 4.91 2.04 4.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Tridecane</td>
<td>5.34 4.99 2.16 5.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>7.33 6.83 4.02 6.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**TABLE 3-8:** The predicted vaporization enthalpy using PR EOS with different alpha functions (continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>%AAD for each model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>n-Pentadecane</td>
<td>6.40</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>8.40</td>
</tr>
<tr>
<td>n-Heptadecane</td>
<td>8.38</td>
</tr>
<tr>
<td>n-Eicosane</td>
<td>5.54</td>
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<tr>
<td>n-Tetracosane</td>
<td>4.82</td>
</tr>
<tr>
<td>n-Octacosane</td>
<td>1.33</td>
</tr>
<tr>
<td>n-Triacontane</td>
<td>4.81</td>
</tr>
<tr>
<td>n-Hentriacontane</td>
<td>7.56</td>
</tr>
<tr>
<td>n-Tetratriacontane</td>
<td>6.65</td>
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<tr>
<td>n-Pentatriacontane</td>
<td>7.19</td>
</tr>
<tr>
<td>n-Hexatriacontane</td>
<td>9.37</td>
</tr>
<tr>
<td>n-Tritetracontane</td>
<td>17.26</td>
</tr>
<tr>
<td>Overall</td>
<td>4.40</td>
</tr>
</tbody>
</table>
hydrocarbons (up to \(n\)-tritetraccontane). It is found that the acentric factor defined at a reduced temperature of 0.6 significantly improves vapour pressure predictions for all the alpha functions evaluated in this study. In addition, the newly developed alpha function has been applied to predict the enthalpy of vaporization of various compounds considered in this study with good accuracy. The modified alpha function obtained in this study leads to the best performance in comparison to either the logarithm-type or Soave-type alpha functions in the literature.
CHAPTER 4 ENHANCED SWELLING EFFECT AND VISCOSITY REDUCTION OF SOLVENT(S)-CO₂-HEAVY OIL SYSTEMS

4.1 Introduction

CO₂ has been found to be an efficient agent for recovering heavy oil resources worldwide through an immiscible displacement process (Tuzunoglu and Bagci, 2000). In a CO₂ immiscible flooding process, oil recovery is enhanced with CO₂ mainly by the following two mechanisms (Al-Abri and Amin, 2010). The most important mechanism is that the lowered crude viscosity due to dissolution of CO₂ in heavy oil results in a reduced average oil saturation by the displacing water. Secondly, dissolution of CO₂ into the oil results in an increased oil volume and a reduced interfacial tension (IFT), and then enhanced production occurs as the reservoir fluid saturations react to accommodate the swollen oil. One major disadvantage associated with CO₂ immiscible process is the limited solubility of CO₂ in heavy oil, resulting in limited swelling effect and viscosity reduction of the CO₂-saturated heavy oil. Addition of alkane solvents (e.g., C₃H₈ and n-C₄H₁₀) to the CO₂ stream may enhance performance of CO₂ dissolution in heavy oil. It is essential that swelling effect and viscosity reduction be significantly enhanced for recovering heavy oil in hydrocarbon reservoirs where other EOR methods are not applicable.

In this study, techniques have been developed to examine the advanced swelling effect and viscosity reduction of CO₂-saturated heavy oil with addition of either C₃H₈ or n-C₄H₁₀. Experimentally, the enhanced swelling factor of CO₂-heavy oil systems due to addition of either C₃H₈ or n-C₄H₁₀ is determined. Theoretically, based on the
experimental phase behaviour data in the literature, three binary interaction parameter (BIP) correlations in the PR EOS (Peng and Robinson, 1976) are used for characterizing CO₂-heavy oil systems, C₃H₈-heavy oil systems, and n-C₄H₁₀-heavy oil systems, respectively. The PR EOS together with the BIP correlations are used to predict the saturation pressures and swelling factors of the C₃H₈-CO₂-heavy oil system and n-C₄H₁₀-CO₂-heavy oil system measured in this study.

4.2 Experimental

4.2.1. Materials

A heavy oil sample is collected from the Lloydminster area in Saskatchewan, Canada. The molecular weight of the Lloydminster heavy oil is measured to be 482 g/mol with a freezing point depression method. The compositional analysis result of the Lloydminster heavy oil is obtained by using the simulated distillation method and provided in TABLE 4-1. It can be seen from TABLE 4-1 that there is no hydrocarbon components lighter than C₉. TABLE 4-2 shows the results of SARA (saturates, aromatics, resins, and asphaltenes) fraction analysis by using an extraction method with alumina. The gas solvents, CO₂, C₃H₈ and n-C₄H₁₀ (Praxair, Canada), used in the measurements have purities of 99.998 mol%, 99.99 wt%, and 99.5 wt%, respectively. It should be noted that the liquid-phase n-C₄H₁₀ is originally compressed in a high pressure cylinder. The high pressure cylinder allows for direct withdrawal of liquid n-C₄H₁₀ from the cylinder. In comparison, only gaseous CO₂ and C₃H₈ can be released from the cylinders and need to be compressed into a liquid phase prior to being injected into the PVT cell.
TABLE 4-1: Compositional analysis result of the Lloydminster heavy oil

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>wt%</th>
<th>mol%</th>
<th>Assumed MW*, g/mol</th>
<th>Carbon No.</th>
<th>wt%</th>
<th>mol%</th>
<th>Assumed MW*, g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0</td>
<td>0</td>
<td>16 C31</td>
<td>1.390</td>
<td>1.42</td>
<td>436</td>
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</tr>
<tr>
<td>C2</td>
<td>0</td>
<td>0</td>
<td>30 C32</td>
<td>1.329</td>
<td>1.31</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>0</td>
<td>0</td>
<td>44 C33</td>
<td>0.981</td>
<td>0.94</td>
<td>464</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>0</td>
<td>0</td>
<td>58 C34</td>
<td>1.083</td>
<td>1.01</td>
<td>478</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>0</td>
<td>0</td>
<td>72 C35</td>
<td>1.307</td>
<td>1.18</td>
<td>492</td>
<td></td>
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<tr>
<td>C6</td>
<td>0</td>
<td>0</td>
<td>86 C36</td>
<td>1.343</td>
<td>1.18</td>
<td>506</td>
<td></td>
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<tr>
<td>C7</td>
<td>0</td>
<td>0</td>
<td>100 C37</td>
<td>0.917</td>
<td>0.78</td>
<td>520</td>
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<tr>
<td>C8</td>
<td>0</td>
<td>0</td>
<td>114 C38</td>
<td>0.900</td>
<td>0.75</td>
<td>534</td>
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<tr>
<td>C9</td>
<td>0.786</td>
<td>2.73</td>
<td>128 C39</td>
<td>1.583</td>
<td>1.29</td>
<td>548</td>
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<tr>
<td>C10</td>
<td>0.844</td>
<td>2.64</td>
<td>142 C40</td>
<td>1.600</td>
<td>1.27</td>
<td>562</td>
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<tr>
<td>C11</td>
<td>1.037</td>
<td>2.96</td>
<td>156 C41</td>
<td>0.750</td>
<td>0.58</td>
<td>576</td>
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<tr>
<td>C12</td>
<td>1.267</td>
<td>3.32</td>
<td>170 C42</td>
<td>0.830</td>
<td>0.63</td>
<td>590</td>
<td></td>
</tr>
<tr>
<td>C13</td>
<td>1.817</td>
<td>4.39</td>
<td>184 C43</td>
<td>1.380</td>
<td>1.02</td>
<td>604</td>
<td></td>
</tr>
<tr>
<td>C14</td>
<td>1.950</td>
<td>4.38</td>
<td>198 C44</td>
<td>0.929</td>
<td>0.67</td>
<td>618</td>
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<tr>
<td>C15</td>
<td>2.300</td>
<td>4.83</td>
<td>212 C45</td>
<td>0.929</td>
<td>0.65</td>
<td>632</td>
<td></td>
</tr>
<tr>
<td>C16</td>
<td>2.143</td>
<td>4.22</td>
<td>226 C46</td>
<td>0.700</td>
<td>0.48</td>
<td>646</td>
<td></td>
</tr>
<tr>
<td>C17</td>
<td>2.286</td>
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<td>240 C47</td>
<td>0.833</td>
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<td>660</td>
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</tr>
<tr>
<td>C18</td>
<td>2.238</td>
<td>3.92</td>
<td>254 C48</td>
<td>0.792</td>
<td>0.53</td>
<td>674</td>
<td></td>
</tr>
<tr>
<td>C19</td>
<td>2.048</td>
<td>3.40</td>
<td>268 C49</td>
<td>0.792</td>
<td>0.51</td>
<td>688</td>
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<tr>
<td>C20</td>
<td>1.857</td>
<td>2.93</td>
<td>282 C50</td>
<td>0.733</td>
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<td>702</td>
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<tr>
<td>C21</td>
<td>2.071</td>
<td>3.11</td>
<td>296 C51</td>
<td>0.750</td>
<td>0.47</td>
<td>716</td>
<td></td>
</tr>
<tr>
<td>C22</td>
<td>1.329</td>
<td>1.91</td>
<td>310 C52</td>
<td>0.717</td>
<td>0.44</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>C23</td>
<td>1.743</td>
<td>2.39</td>
<td>324 C53</td>
<td>0.717</td>
<td>0.43</td>
<td>744</td>
<td></td>
</tr>
<tr>
<td>C24</td>
<td>1.571</td>
<td>2.07</td>
<td>338 C54</td>
<td>0.683</td>
<td>0.40</td>
<td>758</td>
<td></td>
</tr>
<tr>
<td>C25</td>
<td>1.714</td>
<td>2.17</td>
<td>352 C55</td>
<td>0.650</td>
<td>0.37</td>
<td>772</td>
<td></td>
</tr>
<tr>
<td>C26</td>
<td>1.600</td>
<td>1.95</td>
<td>366 C56</td>
<td>0.650</td>
<td>0.37</td>
<td>786</td>
<td></td>
</tr>
<tr>
<td>C27</td>
<td>1.583</td>
<td>1.85</td>
<td>380 C57</td>
<td>0.667</td>
<td>0.37</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>C28</td>
<td>1.650</td>
<td>1.86</td>
<td>394 C58</td>
<td>0.667</td>
<td>0.36</td>
<td>814</td>
<td></td>
</tr>
<tr>
<td>C29</td>
<td>1.452</td>
<td>1.58</td>
<td>408 C59</td>
<td>0.667</td>
<td>0.36</td>
<td>828</td>
<td></td>
</tr>
<tr>
<td>C30</td>
<td>1.281</td>
<td>1.35</td>
<td>422 C60+</td>
<td>36.164</td>
<td>15.01</td>
<td>1072</td>
<td></td>
</tr>
</tbody>
</table>

*Note: The assumed MWs are from Saskatchewan Research Council (SRC).
**TABLE 4-2:** SARA fraction analysis of the Lloydminster heavy oil

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturates</td>
<td>26.2</td>
</tr>
<tr>
<td>Aromatics</td>
<td>28.2</td>
</tr>
<tr>
<td>Resins</td>
<td>24.2</td>
</tr>
<tr>
<td>Asphaltenes</td>
<td>21.4</td>
</tr>
</tbody>
</table>
4.2.2. Viscosity measurements

*Ambient conditions:* Viscosities of the heavy oil samples at the atmospheric pressure and a temperature range of 298.85 K to 373.15 K were measured by using a cone-plate viscometer (DV-II+, Brookfield Engineering Laboratories, USA). The viscometer has a measurement accuracy of 1.0% of the full scale range. The constant temperature during the viscosity measurement is maintained by using a heated circulating water bath (Haake DC10, Thermo Electron Corporation, USA) with an accuracy of ±0.1 K. The spindle CP-51, which covers the viscosity range of 2.4-48000.0 cP, is used in the measurement. The measured viscosity data for the heavy oil sample are tabulated in TABLE 4-3. A two-parameter double logarithm relation has been applied to fit the measured viscosity data,

\[ \log_{10} \left[ \log_{10} (\mu) \right] = -3.7042 \log_{10} (T) + 9.7600 \]  \[ 4-1 \]

where \( \mu \) is the heavy oil viscosity in cP and \( T \) is the temperature in K. The fit produces a correlation coefficient of \( R^2=0.9998 \).

*Reservoir conditions:* It is a challenge to determine viscosity of the solvent-saturated heavy oil at a high pressure, which can be measured with either the expensive commercial in-line viscometers or the capillary viscometer (Memon *et al.*, 2010). After comparing these two options, Memon *et al.* (2010) concluded that the capillary viscometer is a better choice as the capillary viscometer honours more the bulk flow characteristics of a solvent-saturated heavy oil sample. In this study, a customized-capillary viscometer is constructed and connected to the PVT cell for more accurately determining viscosity of the solvent(s)-saturated heavy oil.
**TABLE 4-3:** Measured viscosity of the Lloydminster heavy oil at different temperatures

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.15</td>
<td>8251.0</td>
</tr>
<tr>
<td>303.15</td>
<td>5120.0</td>
</tr>
<tr>
<td>308.15</td>
<td>2977.0</td>
</tr>
<tr>
<td>313.15</td>
<td>1941.0</td>
</tr>
<tr>
<td>318.15</td>
<td>1238.0</td>
</tr>
<tr>
<td>323.15</td>
<td>825.1</td>
</tr>
<tr>
<td>328.15</td>
<td>556.5</td>
</tr>
<tr>
<td>333.15</td>
<td>395.0</td>
</tr>
<tr>
<td>338.15</td>
<td>287.0</td>
</tr>
<tr>
<td>343.15</td>
<td>206.3</td>
</tr>
<tr>
<td>348.15</td>
<td>159.7</td>
</tr>
<tr>
<td>353.15</td>
<td>127.7</td>
</tr>
<tr>
<td>358.15</td>
<td>97.7</td>
</tr>
<tr>
<td>363.15</td>
<td>80.5</td>
</tr>
</tbody>
</table>
The capillary tube is a 3 m long stainless steel tubing (Swagelok, Canada) with an inner diameter (ID) of 0.069 in (0.175 cm) and a wall thickness of 0.028 in (0.071 cm).

The automatic positive displacement pump (PMP-0500-1-10-MB-316-M4-C0, DBR, Canada) is used to displace the solvent(s)-saturated heavy oil from the PVT cell into the capillary tubing. A back-pressure regulator (BPR) (EB1HP1, Equilibar, USA) is used to maintain its outlet pressure at a desirable point, while a differential pressure transducer (P61, Validyne, USA) is used to measure the pressure drop along the tubing.

Two standard viscosity fluids, i.e., S60 and S20 (Cannon Instrument Company, USA), are used as standard viscosity liquids and injected through the capillary tubing at different injection rates to calibrate the capillary viscometer. The injection rates during calibration are controlled below the flow rates that can induce turbulent flow behaviour. The capillary viscometer is calibrated in the temperature range of 294.15 to 321.55 K and pressure range of 101.3 kPa to 5000.0 kPa by using S60 as well as in the temperature range of 294.15 to 321.85 K and pressure range of 101.3 kPa to 5000.0 kPa by using S20. S60 has viscosities of 132.1 cP at 294.15 K and 32.7 cP at 321.55 K, respectively.

FIGURE 4-1 shows effect of BPR pressure on the measured differential pressures across the capillary viscometer at different flow rates for viscosity standards S60 and S20, respectively. Because the viscosity data for the viscosity standard S60 or S20 at pressures higher than 101.3 kPa are not available, constant viscosity is assumed to be valid at a given temperature and in the pressure range of 101.3 kPa to 5000.0 kPa. This assumption is well supported by FIGURE 4-1. As can be seen in FIGURE 4-1, the measured differential pressures follow a good linear relationship with the flow rates. This implies that a constant $k$ value is accurate to represent the viscosity in the pressure range of 101.3
FIGURE 4-1: Effect of BPR pressure on the measured differential pressures across the capillary viscometer at different flow rates for (a) viscosity standard S60; and (b) viscosity standard S20
kPa to 5000.0 kPa at a given temperature, and pressures in the range of 101.3 kPa to 5000.0 kPa have a minor effect on the viscosity of liquid materials.

In practice, at a relatively low pressure, which is often lower than 10000.0 kPa for heavy oil applications, change of pressure in the range of 101.3 kPa to 10000.0 kPa on the single-phase liquid materials imposes a minor effect on the viscosity (Nagashima, 1977; Vogel et al., 1998; Younglove and Ely, 1987). FIGURE 4-2 shows effect of pressure on the water viscosity and C\(_3\)H\(_8\) viscosity at different temperatures, respectively. As can be seen from FIGURE 4-2, at pressures lower than 30000.0 kPa, change of pressure shows only a minor effect on the measured viscosity. Again, although the viscosity data for S60 and S20 at high pressures are not available, it is reasonable to consider that the effect of pressure change in the range of 101.3 kPa to 10000.0 kPa on the liquid-phase S60 and S20 can be neglected.

FIGURE 4-3 shows effect of temperature on the calculated \( k \) constant of the capillary viscometer. It can be seen that the \( k \) constant is slightly reduced at a higher temperature. The degree of reduction for viscosity standard S60 is smaller than that for viscosity standard S20. A linear regression of \( k \) values as a function of temperature is applied by taking into account all the measured \( k \) values at different temperatures and pressures for S60 and S20. The following simplified Poiseuille equation is obtained for the capillary tube used in this study,

\[
\mu = k \frac{\Delta P}{Q} = (14.3671 - 0.0324T) \frac{\Delta P}{Q} \tag{4-2}
\]

where \( k \) is a temperature-dependant characteristic factor, \( \Delta P \) is differential pressure in kPa, and \( Q \) is flow rate in cm\(^3\)/min. The capillary viscometer has an overall accuracy of \( \pm 6.0\% \).
FIGURE 4-2: Effect of pressure on the water viscosity and C$_3$H$_8$ viscosity at different temperatures, respectively (Nagashima, 1977; Vogel et al., 1998; Younglove and Ely, 1987)
FIGURE 4-3: Effect of temperature on the calculated $k$ constant of the capillary viscometer
As for the PVT measurements, viscosity of saturated CO$_2$, C$_3$H$_8$ and $n$-C$_4$H$_{10}$ can be determined from correlations in the following form (Yaws, 2003), respectively.

$$\log_{10}(\mu_s) = d + \frac{e}{T} + fT + gT^2$$ \[4-3\]

where $\mu_s$ is the viscosity of the liquid solvent in cP, $d$, $e$, $f$ and $g$ are the coefficients with the corresponding values for CO$_2$, C$_3$H$_8$ and $n$-C$_4$H$_{10}$ listed in TABLE 4-4. It should be noted that Equation [4-3] is only valid at temperatures below the critical value for a given solvent.

4.2.3. Density measurements

Densities of the heavy oil at a pressure range of 600.0 to 12600.0 kPa and a temperature range of 298.15 K to 348.15 K are measured by using a densitometer (DMA512P, Anton Paar, USA) with a repeatability of $1 \times 10^{-5}$ g/cm$^3$. Prior to density measurement, the densitometer needs to be calibrated within the temperature and pressure range of interest. The densitometer has been calibrated by using deionized water as the test medium in a temperature range of 298.15 K to 348.15 K and a pressure range of 600.0-12600.0 kPa, respectively. At a given temperature and pressure, the oscillation period of density sensor can be recorded. The reference densities of water at various temperatures and pressures are found from the property tables summarized by Wagner and Pruß (2002). Then a calibration formula which correlates water density with pressure, temperature and oscillation period can be developed. Hence, density of a heavy oil sample can be calculated via the calibration equation by reading the oscillation period from the densitometer at a given temperature and a specified pressure.
**TABLE 4-4:** The coefficient values in Equations [4-3] and [4-6]

<table>
<thead>
<tr>
<th>Gas</th>
<th>d</th>
<th>e</th>
<th>f</th>
<th>g</th>
<th>h</th>
<th>l</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>-19.4920</td>
<td>1594.8000</td>
<td>0.0793</td>
<td>-1.2025E-04</td>
<td>0.4638</td>
<td>0.2616</td>
<td>0.2903</td>
</tr>
<tr>
<td>C3H8</td>
<td>-3.1759</td>
<td>297.1200</td>
<td>0.0095</td>
<td>-1.8781E-05</td>
<td>0.2215</td>
<td>0.2774</td>
<td>0.2870</td>
</tr>
<tr>
<td>n-C4H10</td>
<td>-6.8590</td>
<td>673.9300</td>
<td>0.0220</td>
<td>-3.0686E-05</td>
<td>0.2283</td>
<td>0.2724</td>
<td>0.2863</td>
</tr>
</tbody>
</table>
A high-precision syringe pump (500HP, ISCO Inc., USA) applies a given pressure to the cylinder that contains the Lloydminster heavy oil sample. The heated circulating water bath (Haake DC10, Thermo Electron Corporation, USA) is also used to maintain a constant temperature environment for the densitometer. In this study, the well-known Tait equation is used to reproduce the measured heavy oil density data (Goncalves et al., 2010),

\[
\rho_o(T, P) = \frac{\rho_o(T, P_0)}{1 - \beta \ln \left( \frac{B + 0.001P}{B + 0.1} \right)} 
\]

where

\[
\rho_o(T, P_0) = 784.0044 + 1.7217T - 3.3752 \times 10^{-3}T^2 \quad [4-5a]
\]

\[
\beta = (-6.1774 + 0.0213T) \quad [4-5b]
\]

\[
B = 3.7614 \times 10^4 - 1.8009 \times 10^7 T^{-1} + 2.0605 \times 10^9 T^{-2} \quad [4-5c]
\]

where \( \rho \) is the heavy oil density in kg/m\(^3\) and \( P \) is pressure in kPa. The values of the coefficients in the above equations are determined by regressing the heavy oil density data. The fit is accurate with a correlation coefficient of \( R^2=0.9999 \). FIGURE 4-4 shows the comparison of the measured and calculated density of Lloydminster heavy oil.

Density of the saturated CO\(_2\), C\(_3\)H\(_8\) and \( n \)-C\(_4\)H\(_{10}\) can be determined from correlations in the following form (Yaws, 2003), respectively.
FIGURE 4-4: Comparison of the measured and calculated density of Lloydminister heavy oil
\[
\log_{10} \left( \frac{\rho_s}{1000} \right) = \log_{10} (h) - \log_{10} (l) \left( 1 - \frac{T}{T_c} \right)^n
\]  

where \( \rho_s \) is the density of the liquid solvent in kg/m\(^3\), \( T_c \) is the critical temperature of the solvent, \( h, l \) and \( n \) are the coefficients with the corresponding values for CO\(_2\), C\(_3\)H\(_8\) and \( n \)-C\(_4\)H\(_{10}\) listed in TABLE 4-4. It should be noted that Equation [4-6] is only valid at temperatures below the critical value for a given solvent. Comparison of the calculated saturated-densities and viscosities for CO\(_2\), C\(_3\)H\(_8\) and \( n \)-C\(_4\)H\(_{10}\) via Equations [4-3] and [4-6] and the measured data in the literature (Younglove and Ely, 1987) indicates an excellent agreement (See FIGURE 4-5), justifying the use of Equations [4-3] and [4-6].

4.2.4. PVT measurements

In this study, the saturation pressures and swelling factors of 12 solvent(s)-CO\(_2\)-heavy oil systems have been experimentally measured by using the PVT system. The compositions of these 12 feeds are displayed in TABLE 4-5. All the PVT measurements for the solvent(s)-CO\(_2\)-heavy oil systems are performed by using a mercury-free DBR PVT system (PVT-0150-100-200-316-155, DBR, Canada). FIGURE 4-6 is a schematic diagram of the DBR PVT system together with a customized capillary viscometer. The major component of this system is a visual, high-pressure PVT cell, where fluid samples are encapsulated inside a glass tube. The glass tube has an inner diameter of 3.177 cm and a total length of 20.320 cm. In addition to the Heise pressure gauge used in the PVT system, a high-precision test gauge (2089, Ashcroft, USA) with an accuracy of 0.05% full scale of 13789.5 kPa (2000 psia), as indicated in FIGURE 4-6, is attached to the inlet tubing of the PVT cell for more accurate reading of the cell pressure.

The PVT cell has a maximum sample volume of 130 cm\(^3\), while it can sustain
### TABLE 4-5: Compositions of the C₃H₈-\textit{n}-C₄H₁₀-CO₂-heavy oil mixtures tested

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>\textbf{Composition, wt%}</th>
<th>\textbf{Composition, mol%}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>\textbf{C₃H₈}</td>
<td>\textbf{\textit{n}-C₄H₁₀}</td>
</tr>
<tr>
<td>1</td>
<td>11.5</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>14.8</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>20.9</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>11.4</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>19.8</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>29.3</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>15.8</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>0.0</td>
<td>16.4</td>
</tr>
<tr>
<td>9</td>
<td>0.0</td>
<td>36.2</td>
</tr>
<tr>
<td>10</td>
<td>14.2</td>
<td>5.3</td>
</tr>
<tr>
<td>11</td>
<td>10.3</td>
<td>0.0</td>
</tr>
<tr>
<td>12</td>
<td>0.0</td>
<td>10.1</td>
</tr>
</tbody>
</table>
FIGURE 4-5: Comparison of the calculated saturated-densities and viscosities via Equations [4-3] and [4-6] and the measured data (Younglove and Ely, 1987; Vesovic et al., 1990; Span and Wagner, 1996) for (a) CO$_2$, (b) C$_3$H$_8$ and (c) n-C$_4$H$_{10}$, respectively.
FIGURE 4-6: Schematic diagram of experimental setup for conducting the PVT measurements for solvent(s)-CO$_2$-heavy oil systems
pressures up to 69000.0 kPa and its working temperature ranges from 238.15 K to 473.15 K. Inside the glass tube, the fluid samples are isolated from the hydraulic oil by a moveable isolation piston. The cell pressure can be readily varied by using a high-pressure automatic positive-displacement pump (PMP-0500-1-10-MB-316-M4-C0, DBR, Canada) so as to move the floating piston downward or upward. A video-based digital cathetometer with a measurement resolution of 0.002 cm allows direct and accurate measurements of the cell volume. The PVT cell is also equipped with a magnetically coupled mixer, which can be used to effectively mix the fluid system when the fluid viscosity is lower than 100 cP at 298.15 K. The PVT cell and three sample cylinders used to pressurize heavy oil, CO₂ and C₃H₈, respectively, are housed inside a constant-temperature air bath. The air bath temperature is controlled to be accurate within ±0.1 K by using a microprocessor-based controller in conjunction with a resistance temperature device (RTD) sensor.

A fairly high pressure is required when injecting heavy oil sample from the cylinder into the PVT cell due to the long tubing used in the original DBR PVT system. It also needs strenuous effort to cleanse the heavy oil left in the long tubing. In order to enable the PVT system to more easily handle heavy oil sample, a customized-injection tubing assembly with a minimized length is adopted in this study (See FIGURE 4-6).

**Saturation pressure and swelling factor:** Prior to each test, the PVT cell and fluid handling tubing are thoroughly cleaned with kerosene, flushed with air and finally evacuated to remove any traces of the kerosene and air. Prior to each measurement, the temperature of the air bath is set to the desired value for 12 h so that the sample cylinders and the PVT cell are able to reach the preset constant temperature.
In order to expedite the mass transfer process between gas solvent and heavy oil, solvents (i.e., CO$_2$ and C$_3$H$_8$) are firstly compressed into liquid phase in the transfer cylinders, while liquid $n$-C$_4$H$_{10}$ can be directly released from the gas cylinder. As for pure solvent-heavy oil systems, the experimental procedure is briefly described as follows.

The density of a liquid solvent in the PVT cell is calculated via Equation [4-6], while the volume of the liquid solvent is measured by using the cathetometer. Consequently, the mass of solvent injected can be obtained. The magnetic mixer is turned on after solvent injection. A certain amount of heavy oil is then added to the PVT cell by maintaining a constant pressure inside the PVT cell, ensuring the mixture is in the liquid phase. The volume of heavy oil added is determined to be the total volume reading from the cathetometer minus the solvent volume, assuming that there is no volume change due to the mixing of solvent and heavy oil since the volume measurement is conducted right after the heavy oil is injected into the PVT cell. The mass of heavy oil added can be then determined by calculating its density via Equation [4-6]. The solvent-heavy oil mixture is vigorously stirred for 6 h prior to any further measurement.

As for solvent mixture and heavy oil systems, the liquefied solvent with a lower vapour pressure is firstly introduced into the PVT cell. Then another liquefied solvent with a higher vapour pressure is injected into the PVT cell with a pressure just over its vapour pressure. The mass of the second solvent injected can be determined from the volume reading and density equation again. Subsequently, measurement of the bubble-point pressure for the mixture is further conducted to examine the accuracy of the solvent mixture composition. In this study, there exists a good agreement between the measured bubble-point pressure and the value calculated by using PR EOS. Heavy oil is finally
added to the solvent mixture with the pressure maintained just above the saturation pressure of the solvent mixture so that the expected overall composition can be achieved (Badamchi-Zadeh et al., 2009b).

In general, two methods have been made available for determining the saturation pressure of solvent-heavy oil systems, i.e., continuous depressurization method (Badamchi-Zadeh et al., 2009a; Memon et al., 2010) and discrete depressurization method (Badamchi-Zadeh et al., 2009a). A pressure-volume relationship curve can be obtained for either of the two methods. The saturation pressure is conventionally determined by locating the transitioning point on the pressure-volume curve. It is worth noting that, as for both methods, the magnetic stirrer is always kept on to rigorously stir the solvent and heavy oil mixtures in order to significantly shorten the time for the mixture to reach its equilibrium state.

As for the continuous depressurization method, the solvent(s)-heavy oil mixture is depressurized starting from liquid state at a low-enough withdrawal rate while keeping the magnetic mixer on. As for the discrete depressurization method, prior to any volume and pressure readings, the mixture is depressurized step by step while keeping the magnetic mixer on. Long-enough equilibration time is allowed for each step until the pressure inside the PVT cell reaches a stable value. The discrete depressurization method is considered to be more accurate since it can mitigate the supersaturation phenomenon that would otherwise occur in the continuous depressurization method (Badamchi-Zadeh et al., 2009a). In this study, both methods are tested and compared. For the continuous depressurization method, a withdrawal rate of 3 cm³/h is used, while for the discrete depressurization method, 12 h are found to be adequate for the system pressure to reach a
stable value and hence allotted to each step. It is worthwhile noting that both the saturation pressure and the mixture volume at the saturation pressure can be read from the transitioning point on the pressure-volume curve. Consequently, the swelling factor of the heavy oil at a given temperature can be determined to be the mixture volume at saturation point divided by the volume of heavy oil at atmospheric pressure and the given temperature.

**Viscosity of the solvent(s)-saturated heavy oil:** Prior to each viscosity measurement, the capillary tubing is cleaned with kerosene, flushed with air for 4 h, and finally vacuumed. The whole capillary viscometer setup is also placed in the PVT air bath to ensure it has the same temperature as the PVT cell. The BPR pressure is set at a pre-specified value which is well above the measured saturation pressure of a given solvent(s)-heavy oil mixture to prevent the occurrence of gas-liquid two-phase flow in the capillary tube. A high-accuracy syringe pump (500HP, Teledyne ISCO Inc., USA) is used to apply pressure on the BPR. After each saturation pressure measurement, the solvent(s)-saturated heavy oil is displaced into the capillary tubing by using the automatic displacement pump at a given flow rate. The differential pressure reading is recorded once it reaches a stable value. Then Equation [4-2] is then used to determine the viscosity of the solvent(s)-saturated heavy oil. In this study, the viscosity measurements are performed for the C\textsubscript{3}H\textsubscript{8}-heavy oil system, \textit{n}-C\textsubscript{4}H\textsubscript{10}-heavy oil system, and \textit{n}-C\textsubscript{4}H\textsubscript{10}-CO\textsubscript{2}-heavy oil system at 298.85 K, and the C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2}-heavy oil system at 318.75 K, respectively.
In this study, the pressure measurement, volume measurement, temperature measurement, determination of mixture composition, and viscosity measurement have uncertainties of ±6.9 kPa, ±1.59×10^{-2} cm^3, ±0.1 K, ±3.0 wt%, and ±6.0%, respectively.

4.3 Mathematical Formulation

4.3.1. PR EOS model

Due to its wide application in the petroleum and chemical industries, the PR EOS is chosen as the equation of state for describing phase behaviour of solvent(s)-CO\textsubscript{2}-heavy oil systems. The detailed expressions of the PR EOS can be found in CHAPTER 3 of this dissertation. The new alpha function for the PR EOS is used to more accurately predict the low vapour pressures for heavy hydrocarbons. The new alpha function is expressed by,

\[
\alpha = \exp \left\{ (0.13280 - 0.05052 \omega + 0.25948 \omega^2)(1-T_r) + 0.81769 \ln \left[ 1 + (0.31355 + 1.86745 \omega - 0.52604 \omega^2)(1-\sqrt{T_r})^2 \right] \right\}
\]

[4-7]

For a mixture system, the following van der Waals mixing rule is used,

\[
a = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j (1-\delta_{ij}) \sqrt{a_i a_j}
\]

[4-8]

\[
b = \sum_{i=1}^{nc} x_i b_i
\]

[4-9]

where \( nc \) is number of components in the mixture, \( x_i \) is mole fraction of the \( i \)th component in the mixture, \( a_i \) and \( b_i \) are calculated from Equations [3-2] and [3-4] for the \( i \)th component, respectively, and \( \delta_{ij} \) is BIP between the \( i \)th component and the \( j \)th component.
In this study, molar volume of the liquid or vapour phase is calculated with a volume-translation strategy. In a volume-translated PR EOS framework, the corrected molar volume is simply related to the EOS-calculated molar volume by (Peneloux et al., 1982),

\[ V_{\text{corrected}} = V - C \]  \[4-10\]

where \( V_{\text{corrected}} \) is corrected molar volume, \( V \) is original molar volume calculated by the PR EOS, and \( C \) is a component-specific correction factor. The correction factor of a pure component is given as follows (Peneloux et al., 1982),

\[ C = 0.40768 \left( \frac{R T_c}{P_c} \right) (0.29441 - Z_{RA}) \]  \[4-11\]

where \( Z_{RA} \) is Rackett parameter that is a constant for a given substance. The Rackett parameter of a heavy oil sample can be calculated by applying the following equation at 60°F (Spencer and Danner, 1972),

\[ V^* = \frac{R T_c}{P_c} Z_{RA} \left[ 1 + \frac{(1 - T_c^*)^2}{2} \right] = \frac{MW}{SG} \]  \[4-12\]

where \( V^* \) is molar volume of heavy oil at 60°F, and \( T_c^* \) is reduced temperature evaluated at 60°F. Solving \( Z_{RA} \) from Equation [4-12] results in the Rackett parameter for heavy oil,

\[ Z_{RA} = \left( \frac{MW \cdot P_c}{RT_c \cdot SG} \right)^{\frac{1}{1 + \frac{(1 - T_c^*)^2}{2}}} \]  \[4-13\]

Peneloux et al. (1982) extended Equation [4-10] to a multicomponent mixture by using the following mole-composition based mixing rule,

\[ V_{\text{corrected}} = V - \sum_{i=1}^{n_c} x_i C_i \]  \[4-14\]
By treating each crude oil as a single pseudocomponent and characterizing it with specific gravity and normal boiling point or Watson factor, Mullken and Sandler (1980) proposed a CO₂-heavy oil BIP correlation with a better accuracy for determining both CO₂ solubility and swelling factor of the CO₂-saturated oil. It should be pointed out that normal boiling point or Watson factor is usually unavailable for heavy oil samples. However, molecular weight is a more accessible parameter for heavy oils that are documented in the literature than either normal boiling point or Watson factor.

In this study, each heavy oil sample is also treated as a single pseudocomponent, while specific gravity and molecular weight are used as the two parameters that characterize each heavy oil sample. As recommended by Whitson and Brule (2000), the Soreide correlation (Soreide, 1989) is used to calculate normal boiling point of heavy oil from molecular weight and specific gravity, while the commonly used Kesler-Lee correlations (Lee and Kesler, 1975; Kesler and Lee, 1976) are used to calculate critical properties of heavy oil based on normal boiling point and specific gravity. In addition, more solubility data for CO₂-heavy oil and C₃H₈-heavy oil systems are included in the database for developing the BIP correlations. One reason to characterize heavy oil as one pseudocomponent is to make the model presented in this work predictive in nature.

4.3.2. BIP correlations

Once the heavy oil is characterized by its critical properties, the BIP matrix \( \delta \) remains to be a single parameter that is needed in the PR EOS to model the phase behaviour of solvent(s)-heavy oil systems at given conditions. Three solvents (i.e., CO₂, C₃H₈, and \( n \)-C₄H₁₀) are used in this study. For the purpose of convenience, CO₂, C₃H₈, \( n \)-C₄H₁₀ and heavy oil are designated as Components #1, #2, #3 and #4, respectively.
TABLE 4-6 shows the BIP matrix for a four-component fluid system which is comprised of CO₂, C₃H₈, n-C₄H₁₀ and heavy oil. The fixed δ₁₂ for CO₂-C₃H₈ binary and δ₁₃ for CO₂-n-C₄H₁₀ binary are rigorously reviewed values retrieved from a commercial simulator (Computer Modelling Group, 2009). δ₂₃ for C₃H₈-n-C₄H₁₀ binary is calculated to be 0.00087 by using a hydrocarbon-hydrocarbon BIP correlation (Mehra, 1981).

TABLE 4-7 lists the phase behaviour database for binary CO₂-heavy oil system used for developing δ₁₄ correlation, while TABLE 4-8 shows the database for C₃H₈-heavy oil system used for developing δ₂₄ correlation. The δ₃₄ correlation for n-C₄H₁₀-Lloydminster heavy oil system is developed based on the experimental data measured in this study. The heavy oils that have both specific gravity and molecular weight available are included in the database. The calculated critical properties of each oil sample are also provided in TABLEs 4-7 and 4-8, respectively. For each isotherm solubility data set, the BIP is optimized by minimizing the root-mean-squared relative error (RMSRE) between the measured and calculated solvent solubility in heavy oil,

\[
RMSRE_X = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}} \right)^2}
\]  

where \(X_i^{cal}\) is the calculated solvent solubility in heavy oil, \(X_i^{exp}\) is the measured solvent solubility in heavy oil, and \(N\) is number of data point along each isotherm. Once all the optimum BIPs are obtained for every isotherm of each oil sample, the optimum BIPs are correlated with the following linear equation (Mullken and Sandler, 1980),

\[
\delta = F - G \cdot T_i - H \cdot SG - K \cdot \omega
\]  

where \(F, G, H, K\) are coefficients. The swelling factor of solvent-saturated heavy oil can be calculated via the following equation (Teja and Sandler, 1980),
TABLE 4-6: BIP matrix for the $n$-$C_4H_{10}$-$C_3H_8$-$CO_2$-heavy oil system

<table>
<thead>
<tr>
<th>Component</th>
<th>CO$_2$</th>
<th>C$_3$H$_8$</th>
<th>$n$-$C_4H_{10}$</th>
<th>Heavy oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0.13500</td>
<td>0.13000</td>
<td>$\delta_{14}$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.13500</td>
<td>0</td>
<td>0.00087</td>
<td>$\delta_{24}$</td>
</tr>
<tr>
<td>$n$-$C_4H_{10}$</td>
<td>0.13000</td>
<td>0.00087</td>
<td>0</td>
<td>$\delta_{34}$</td>
</tr>
<tr>
<td>Heavy oil</td>
<td>$\delta_{14}$</td>
<td>$\delta_{24}$</td>
<td>$\delta_{34}$</td>
<td>0</td>
</tr>
</tbody>
</table>
### TABLE 4-7: Database for developing the BIP correlation for CO2-heavy oil systems

<table>
<thead>
<tr>
<th>Oil</th>
<th>MW</th>
<th>SG @ 60°F</th>
<th>$T_c$, K</th>
<th>$P_c$, kPa</th>
<th>$\omega$</th>
<th>Swelling factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Senlac heavy oil</td>
<td>440</td>
<td>0.9718</td>
<td>908.16</td>
<td>1250.17</td>
<td>1.0095</td>
<td>Yes</td>
<td>Strivastava et al., 1999</td>
</tr>
<tr>
<td>A</td>
<td>350</td>
<td>0.9509</td>
<td>861.00</td>
<td>1472.77</td>
<td>0.8831</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>B</td>
<td>236</td>
<td>0.8586</td>
<td>753.01</td>
<td>1689.54</td>
<td>0.7168</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>C</td>
<td>345</td>
<td>0.8586</td>
<td>824.42</td>
<td>1041.61</td>
<td>1.0251</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>D</td>
<td>358</td>
<td>0.9446</td>
<td>862.28</td>
<td>1408.55</td>
<td>0.9100</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>E</td>
<td>463</td>
<td>0.9759</td>
<td>918.26</td>
<td>1203.77</td>
<td>1.0374</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>F</td>
<td>330</td>
<td>0.9854</td>
<td>868.24</td>
<td>1362.96</td>
<td>0.9340</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>G</td>
<td>373</td>
<td>0.8996</td>
<td>852.76</td>
<td>1130.91</td>
<td>1.0164</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>H</td>
<td>458</td>
<td>0.9868</td>
<td>920.44</td>
<td>1268.55</td>
<td>1.0095</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>I</td>
<td>370</td>
<td>0.9452</td>
<td>868.24</td>
<td>1362.96</td>
<td>0.9340</td>
<td>Yes</td>
<td>Simon and Graue, 1965</td>
</tr>
<tr>
<td>Athabasca bitumen</td>
<td>552</td>
<td>1.0070</td>
<td>958.33</td>
<td>1139.11</td>
<td>1.0936</td>
<td>No</td>
<td>Mehrotra and Svrcek, 1982;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Mehrotra and Svrcek, 1985a;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fu et al., 1985</td>
</tr>
<tr>
<td>Wabasca bitumen</td>
<td>446.5</td>
<td>1.0070</td>
<td>924.07</td>
<td>1396.28</td>
<td>0.9589</td>
<td>No</td>
<td>Mehrotra and Svrcek, 1985a</td>
</tr>
<tr>
<td>Saskatchewan oil</td>
<td>423</td>
<td>0.9653$^b$</td>
<td>899.02</td>
<td>1271.37</td>
<td>0.9938</td>
<td>Yes</td>
<td>Jha, 1986</td>
</tr>
<tr>
<td>Cold lake bitumen</td>
<td>533</td>
<td>1.0484</td>
<td>967.49</td>
<td>1373.82</td>
<td>0.9933</td>
<td>No</td>
<td>Mehrotra and Svrcek, 1988;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yu et al., 1989</td>
</tr>
<tr>
<td>Peace river bitumen</td>
<td>542</td>
<td>0.9974$^c$</td>
<td>952.09</td>
<td>1115.30</td>
<td>1.1016</td>
<td>No</td>
<td>Svreck and Mehrotra, 1989</td>
</tr>
<tr>
<td>Lindbergh heavy oil</td>
<td>490</td>
<td>0.9678</td>
<td>925.07</td>
<td>1096.63</td>
<td>1.0930</td>
<td>No</td>
<td>Sayegh et al., 1990</td>
</tr>
<tr>
<td>Suffield heavy oil$^d$</td>
<td>358</td>
<td>0.9533</td>
<td>865.82</td>
<td>1450.10</td>
<td>0.8959</td>
<td>Yes</td>
<td>Kodal and Sayegh, 1992</td>
</tr>
<tr>
<td>West Sask. oil #1</td>
<td>330</td>
<td>0.9433</td>
<td>847.74</td>
<td>1526.89</td>
<td>0.8535</td>
<td>No</td>
<td>DeRuiter et al., 1994</td>
</tr>
<tr>
<td>West Sask. oil #2</td>
<td>446</td>
<td>0.9725</td>
<td>910.70</td>
<td>1235.70</td>
<td>1.0177</td>
<td>No</td>
<td>DeRuiter et al., 1994</td>
</tr>
</tbody>
</table>

Note:

$^a$ These oil are dead oils with a vapour pressure lower than 1 atm.

$^b$ The SG is reported at 68°F.

$^c$ The SG is averaged from the SGs of pseudocomponents reported in the corresponding literature.

$^d$ Solubility data are based on the average of reported data at the top and bottom of mixture.
### TABLE 4-8: Database for developing the BIP correlation for C₃H₈-heavy oil systems

<table>
<thead>
<tr>
<th>Oil</th>
<th>MW</th>
<th>SG @ 60°F</th>
<th>Tₙ, K</th>
<th>Pₙ, kPa</th>
<th>ω</th>
<th>Swelling factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Athabasca bitumen</td>
<td>552</td>
<td>1.0070</td>
<td>958.33</td>
<td>1139.11</td>
<td>1.0936</td>
<td>No</td>
<td>Badamchi-Zadeh et al., 2009a</td>
</tr>
<tr>
<td>Peace river bitumen</td>
<td>542</td>
<td>0.9974</td>
<td>952.09</td>
<td>1115.30</td>
<td>1.1016</td>
<td>No</td>
<td>Das and Butler, 1996</td>
</tr>
<tr>
<td>Winter heavy oil</td>
<td>412</td>
<td>0.9730</td>
<td>897.51</td>
<td>1343.27</td>
<td>0.9654</td>
<td>No</td>
<td>Freitag et al., 2005</td>
</tr>
<tr>
<td>Lloydminster heavy oil</td>
<td>432.33</td>
<td>0.9880</td>
<td>911.38</td>
<td>1349.27</td>
<td>0.9725</td>
<td>Yes</td>
<td>Luo et al., 2007; Luo and Gu, 2007</td>
</tr>
</tbody>
</table>

**Note:**
- The MW is averaged from the MWs of pseudocomponents reported in the literature.
where $SF$ is swelling factor, $V_{s1}$ is molar volume of heavy oil at atmospheric pressure and saturation temperature, $V_{s2}$ is molar volume of solvent-saturated heavy oil at saturation pressure and saturation temperature, and $X$ is solvent solubility in mole fraction.

**CO$_2$-heavy oil systems:** The following BIP correlation is obtained for CO$_2$-heavy oil systems,

$$\delta_{14} = -0.5462 \frac{T}{T_c} - 0.4596 SG - 0.0238 \omega + 0.7523$$

[4-18]

where $SG$, and $\omega$ are specific gravity and acentric factor of heavy oil, respectively. The standard errors of the coefficients in Equation [4-18] are 0.0458, 0.0565, 0.0192 and 0.0626, respectively. Equation [4-18] indicates that the BIP between CO$_2$ and heavy oil has a negative dependence on the reduced temperature. FIGURE 4-7a shows the parity chart of the measured and calculated CO$_2$ solubility by using Equation [4-18]. There exists a good agreement between the measured and calculated CO$_2$ solubility with a percentage absolute average deviation (%AAD) of 7.00% for the 208 solubility data points. In addition, the PR EOS with Equation [4-18] has been applied to predict the swelling factor of the CO$_2$-saturated oils. FIGURE 4-7b shows the parity chart of the measured and calculated swelling factor. As can be seen from FIGURE 4-7b, a very accurate prediction of the swelling factor is achieved with a %AAD of only 1.80% for the 53 data points.

**C$_3$H$_8$-heavy oil systems:** As for the C$_3$H$_8$-heavy oil system, it is found that the BIP shows a weak dependence on specific gravity and acentric factor, but a strong dependence on the reduced temperature. Hence, the following BIP correlation for C$_3$H$_8$-
FIGURE 4-7: Parity chart of the measured and calculated phase behaviour data for CO₂-heavy oil systems by using the PR EOS with Equations [4-7] and [4-18]: (a) CO₂ solubility; and (b) swelling factor of CO₂-saturated heavy oil
heavy oil systems is obtained,

$$\delta_{24} = -0.4560 \frac{T}{T_c} + 0.1817$$  \hspace{1cm} [4-19]$$

The standard errors of the coefficients in Equation [4-19] are 0.1680 and 0.0539, respectively. FIGURE 4-8a shows the parity chart of the measured and calculated C\textsubscript{3}H\textsubscript{8} solubility by using Equation [4-19]. A good agreement exists between the measured and calculated C\textsubscript{3}H\textsubscript{8} solubility with a %AAD of 7.30% for the 65 solubility data points. The PR EOS with Equation [4-19] is also used to predict the swelling factor of the C\textsubscript{3}H\textsubscript{8}-saturated heavy oil (Luo et al., 2007; Luo and Gu, 2009). Comparison between the measured and predicted swelling factor (See FIGURE 4-8b) shows that, in general, the swelling factor increases with an increased equilibrium pressure at a given temperature and decreases with temperature at a given equilibrium pressure. This is mainly attributed to the increased C\textsubscript{3}H\textsubscript{8} solubility at a higher pressure or a lower temperature. Meanwhile, a very accurate prediction of the swelling factor of the C\textsubscript{3}H\textsubscript{8}-saturated heavy oil is also achieved with a %AAD of only 1.70% for the 9 data points.

**n-C\textsubscript{4}H\textsubscript{10}-heavy oil systems:** FIGURE 4-9 shows the optimized BIP for the binary n-C\textsubscript{4}H\textsubscript{10}-heavy oil systems (Feeds #8 and #9) as a function of temperature. In general, the optimized BIP shows a negative dependence on temperature. A BIP correlation similar to Equation [4-19] is also obtained for the n-C\textsubscript{4}H\textsubscript{10}-heavy oil binary based on the phase behaviour data measured in this study,

$$\delta_{34} = -0.2331 \frac{T}{T_c} + 0.1198$$  \hspace{1cm} [4-20]$$

where $\delta_{34}$ is the BIP between n-C\textsubscript{4}H\textsubscript{10} and heavy oil. The fit is generally good with a correlation coefficient of 0.6103. The standard errors of two coefficients in Equation...
FIGURE 4-8: Comparison of the measured and calculated phase behaviour data for C$_3$H$_8$-heavy oil systems by using PR EOS with Equations [4-7] and [4-19]: (a) C$_3$H$_8$ solubility; and (b) swelling factor of C$_3$H$_8$-saturated heavy oil
FIGURE 4-9: The experimentally optimized BIPs and the linearly regressed values for the $n$-C$_4$H$_{10}$-heavy oil binaries (Feeds #8 and #9) as a function of temperature
[4-20] are 0.0589 and 0.0217, respectively. It is noted that Equation [4-20] may be also applicable for other heavy oils, though it has not been tested in this study.

4.3.3. Mixing rules for mixture viscosity

Viscosity of solvent-heavy oil mixtures at a given temperature depends on mixture composition and viscosity of each component. Since it is extremely difficult to quantify the individual contribution of each component in heavy oil to the viscosity of the mixture, heavy oil is usually treated as a single pseudocomponent. Several mixing rules have been developed for estimating the viscosity of solvent-solute mixture. One classical mixing rule (i.e., the log-type mixing rule) is first examined in this study (Yazdani and Maini, 2010). The log-type mixing rule is given as,

$$\log_{10}(\mu_m) = \phi_s \log_{10}(\mu_s) + \phi_o \log_{10}(\mu_o)$$ \hspace{1cm} [4-21]

where \(\mu_m\) is the mixture viscosity, \(\phi_s\) is the volume fraction of solvent, \(\mu_s\) is the solvent viscosity, \(\phi_o\) is the volume fraction of oil, and \(\mu_o\) is the oil viscosity.

Cragoe (1933) developed a widely used method for predicting the liquid mixture viscosity based on the fact that the mixture viscosity is not a simply linear function of the solvent fraction. Mixing rules are used in their model to combine the “Liquidity” \(L\) of the solvent and solute. Liquidity is expressed as,

$$L = \frac{1000 \ln 20}{\ln \mu - \ln \left(5 \times 10^{-4}\right)}$$ \hspace{1cm} [4-22a]

where \(\mu\) is viscosity of the solvent or oil. The mixture liquidity is calculated from the following mixing rule,

$$L_m = w_s L_s + w_o L_o$$ \hspace{1cm} [4-22b]
where $L_m$ is the mixture liquidity, $w_s$ is the weight fraction of solvent, $w_o$ is the weight fraction of oil, and $L_s$ and $L_o$ are the liquidity of solvent and oil, respectively.

Lederer (1933) presented a modified form of the classic Arrhenius expression,

$$
\ln \mu_m = \frac{\phi_s}{\alpha' \phi_s + \phi_o} \ln \mu_s + \left(1 - \frac{\phi_s}{\alpha' \phi_s + \phi_o}\right) \ln \mu_o
$$

[4-23a]

where $\alpha'$ is an empirical constant with a value between 0 and 1. Shu (1984) extended the Lederer equation to higher viscosity ratios by using a generalized expression for the empirical constant $\alpha'$,

$$
\alpha' = \frac{17.04 (\rho_o - \rho_s)^{0.5237} \rho_o^{3.2745} \rho_s^{1.6316}}{\ln \left(\frac{\mu_o}{\mu_s}\right)}
$$

[4-23b]

where $\rho_s$ and $\rho_o$ are specific gravity of the solvent and heavy oil, respectively. This correlation is tested with heavy oil/bitumen-solvent blending data and provides an excellent prediction of the mixture viscosities. However, the correlation developed by Shu is based on organic solvents (e.g., kerosene) and may be not appropriate for CO$_2$-heavy oil systems where CO$_2$ density is higher than that of heavy oil at certain high pressures (Chung et al., 1988). Chung et al. (1988) obtained a modified $\alpha'$ correlation for determining CO$_2$-heavy oil mixture viscosity,

$$
\alpha' = 0.2555G^{-4.16} \left(\frac{1.87T}{547.57}\right)^{1.85} \left[\frac{e^{7.36} - e^{7.36(1-P'/17384)}}{e^{7.36} - 1}\right]
$$

[4-23c]

The following Lobe’s mixing rule is also examined for calculating the viscosity of solvent-diluted crude oil (Lobe, 1973),

$$
v_m = \phi_s v_s \exp(\phi_o \alpha_o) + \phi_o v_o \exp(\phi_s \alpha_s)
$$

[4-24a]

where
\[
\alpha_0 = 0.27 \ln \left( \frac{V_0}{V_s} \right) + \left[ 1.3 \ln \left( \frac{V_0}{V_s} \right) \right]^{0.5} \tag{4-24b}
\]

\[
\alpha_s = -1.7 \ln \left( \frac{V_0}{V_s} \right) \tag{4-24c}
\]

where \( \nu \) is the kinematic viscosity which is related to the dynamic viscosity by \( \mu = \rho \nu \).

### 4.4 Results and Discussion

#### 4.4.1. Validation of the BIP correlations

In order to validate the predictive capability of the proposed BIP correlations, these correlations are tested with the recently published phase behaviour data on three \( \text{C}_3\text{H}_8\)-\( \text{CO}_2\)-Athabasca bitumen mixtures (Badamchi-Zadeh et al., 2009b). It should be pointed out that the phase behaviour data for the three mixtures are not included in the database for developing the BIP correlations. The BIP between \( \text{CO}_2 \) and \( \text{C}_3\text{H}_8 \) is set as 0.13500, while those for \( \text{CO}_2 \)-heavy oil binary and \( \text{C}_3\text{H}_8 \)-heavy oil binary at different temperatures are predicted with Equations [4-18] and [4-19], respectively.

The saturation pressures of the mixtures are calculated by following the procedure provided by Peterson and Christensen (2006). FIGURE 4-10 compares the measured and predicted saturation pressures of the two \( \text{C}_3\text{H}_8\)-\( \text{CO}_2\)-Athabasca bitumen mixtures with different methods. In general, the PR EOS with the BIPs calculated by the proposed correlations is able to accurately reproduce the saturation pressures for the two mixtures. The PR EOS model used in this study is also compared to the advanced PR EOS (APR EOS) model that was recently used by Díaz et al. (2011). It is interesting to note that the PR EOS model, which treats the bitumen as a single pseudocomponent, provides a
FIGURE 4-10: Comparison of the measured saturation pressures (Badamchi-Zadeh et al., 2009b) and calculated values with different models for the ternary mixtures: (a) Mixture #1 (24.0 wt% \( \text{C}_3\text{H}_8 \), 6.2 wt% \( \text{CO}_2 \), 69.8 wt% bitumen); and (b) Mixture #2 (13.5 wt% \( \text{C}_3\text{H}_8 \), 11.0 wt% \( \text{CO}_2 \), 75.5 wt% bitumen)
slightly better prediction accuracy of the L1V boundary as compared to the regressed APR EOS (Díaz et al., 2011) model where the bitumen is treated as a mixture comprised of multi-pseudocomponents. In addition, it can be seen from FIGURE 4-10 that the use of zero BIPs for CO2-bitumen pair and C3H8-bitumen pair cannot reproduce the saturation pressures correctly. This is ascribed to the fact that the BIP has a significant effect on performance of the PR EOS in predicting phase behaviours of heavy oil involved systems.

The L1L2V three phase boundaries of a mixture (13.1 wt% C3H8, 19.2 wt% CO2, 67.7 wt% bitumen) were also reported recently (Badamchi-Zadeh et al., 2009b). In principle, phase boundaries for a multicomponent system with a given feed can be detected by performing stability test and subsequent flash calculations. In this study, the Michelsen’s stability test criteria are adopted to perform the stability test of a given multicomponent system (Michelsen, 1982). FIGURE 4-11 compares the measured three phase boundaries for the mixture with the predicted ones by using the PR EOS with the newly developed BIP correlations and Equation [4-7]. The PR EOS with the BIPs calculated by the newly proposed correlations reproduces well the three phase boundaries, though the PR EOS model used in this study generates a slightly larger error in comparison to the APR EOS model (Díaz et al., 2011) (See FIGURE 4-11).

It should be pointed out herein that there is one underlying drawback that arises from characterizing the heavy oil as a single pseudocomponent in the PR EOS. According to Gibbs’s phase rule, the L1L2V three phase boundaries will be predicted to be a line on the P-T diagram if the CO2-heavy oil system is only characterized by two components, i.e., CO2 and heavy oil. However, the L1L2V three phase boundary of some CO2-heavy oil systems has been found to spread over a small area instead of a line (Kodal and
FIGURE 4-11: Comparison of the measured L\(_1\)L\(_2\)V boundaries (Badamchi-Zadeh et al., 2009b) and calculated ones with the PR EOS used in this study and the APR EOS (Díaz et al., 2011) for Mixture #3 (13.1 wt% C\(_3\)H\(_8\), 19.2 wt% CO\(_2\), 67.7 wt% bitumen)
Sayegh, 1992). Nonetheless, the newly proposed BIP correlations can still be of value as a tool to estimate the three phase boundary of CO\textsubscript{2}-heavy oil systems due to the narrow span of the three phase boundary (Kodal and Sayegh, 1992).

4.4.2. Solvent(s)-Lloydminster heavy oil systems

\textit{C}_3\textit{H}_8-Lloydminster heavy oil system: Six \textit{C}_3\textit{H}_8-Lloydminster heavy oil systems have been tested in this study. FIGURE 4-12 shows the measured typical \textit{P}-\textit{V} relations by using the continuous depressurization method and discrete depressurization method for (a) Feed #3 (20.9 wt\% \textit{C}_3\textit{H}_8, 79.1 wt\% heavy oil) at 298.85 K and (b) Feed #4 (11.6 wt\% \textit{C}_3\textit{H}_8, 88.4 wt\% heavy oil) at 323.85 K, respectively. It can be seen from FIGURE 4-12 that there is a minor difference between the measured \textit{P}-\textit{V} curves by using the continuous depressurization method and discrete depressurization method. Badamchi-Zadeh \textit{et al}. (2009a) also compared the measured \textit{P}-\textit{V} relations by using the above-mentioned methods for a \textit{C}_3\textit{H}_8-Athabasca bitumen system, though a larger discrepancy between them was observed. The minor difference caused by these two methods in this study is probably attributed to the lower viscosity of the Lloydminster heavy oil used, compared to that of the highly viscous Athabasca bitumen. In this study, the continuous depressurization method is subsequently used to perform the saturation pressure and swelling factor measurements for all the solvent(s)-CO\textsubscript{2}-heavy oil systems. TABLE 4-9 summarizes the physical properties of CO\textsubscript{2}, \textit{C}_3\textit{H}_8, \textit{n-C}_{4}\textit{H}_{10} and Lloydminster heavy oil which are used as inputs for the subsequent prediction of saturation pressures and swelling factors.

FIGURE 4-13 shows the measured and predicted saturation pressures and swelling factors for the \textit{C}_3\textit{H}_8-Lloydminster heavy oil systems with Feeds #1-3 at 298.85 K and
### TABLE 4-9: Physical properties of CO₂, C₃H₈, n-C₄H₁₀ and Lloydminster heavy oil

<table>
<thead>
<tr>
<th>Component</th>
<th>Pₑ, kPa</th>
<th>Tₑ, K</th>
<th>ω</th>
<th>Zₑa</th>
<th>Vₑc, m³/kmol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>7378</td>
<td>304.14</td>
<td>0.2238</td>
<td>0.2736</td>
<td>0.0940</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>4246</td>
<td>369.80</td>
<td>0.1520</td>
<td>0.2763</td>
<td>0.2030</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>3786</td>
<td>425.20</td>
<td>0.1930</td>
<td>0.2728</td>
<td>0.2550</td>
</tr>
<tr>
<td>Lloydminster heavy oil</td>
<td>1265</td>
<td>933.66</td>
<td>1.0288</td>
<td>0.2621</td>
<td>1.2460</td>
</tr>
</tbody>
</table>
FIGURE 4-12: $P$-$V$ relations measured by the continuous depressurization method and discrete depressurization method for (a) Feed #3 (20.9 wt% C$_3$H$_8$, 79.1 wt% heavy oil) at 298.85 K; and (b) Feed #4 (11.6 wt% C$_3$H$_8$, 88.4 wt% heavy oil) at 323.85 K
FIGURE 4-13: Measured and predicted saturation pressures and swelling factors for the C₃H₈-Lloydminster heavy oil system (a) Feeds #1-3 at 298.85 K; and (b) Feeds #4-6 at 323.85 K, respectively.
with Feeds #4-6 at 323.85 K, respectively. It can be seen from FIGURE 4-13 that the saturation pressure increases as the solubility of C3H8 in heavy oil increases. The saturation pressure also increases with temperature for the same C3H8 solubility. It is worthwhile noting that dissolution of C3H8 leads to an enhanced swelling effect of the Lloydminster heavy oil. For example, the heavy oil swells around 1.50 times with dissolution of 74.4 mol% (20.9 wt%) of C3H8. A large swelling factor is particularly beneficial for achieving an improved recovery performance of solvent flooding processes. In addition, the PR EOS with Equations [4-7] and [4-19] is able to accurately predict the saturation pressures and swelling factors for the C3H8-Lloydminster heavy oil system.

FIGURE 4-14 compares the measured saturation pressures and swelling factors and their predicted values for the C3H8-Lloydminster heavy oil system: Feed #7. It can be seen from this figure that the saturation pressure increases with temperature. This implies that, at the same pressure, solubility of C3H8 at a higher temperature is smaller than that at a lower temperature. As can also be seen from FIGURE 4-14 the swelling factor for the C3H8-heavy oil binary maintains almost constant at different temperatures. It can be also seen from FIGURE 4-14 that, in general, there exists a generally good agreement between the measured and calculated saturation pressures, though the accuracy is somewhat compromised at a high temperature close to the critical temperature of C3H8. The reduced accuracy at a high temperature might be attributed to the fact that the PR EOS model is less accurate when used for modeling C3H8-heavy oil phase behaviour at temperatures close to the critical temperature of C3H8.

**n-C4H10-Lloydminster heavy oil system**: Two n-C4H10-Lloydminster heavy oil systems have been tested in this study. FIGURE 4-15 compares the measured saturation
FIGURE 4-14: Comparison of the measured saturation pressures and swelling factors and their predicted values for the C$_3$H$_8$-Lloydminster heavy oil binary: Feed #7
FIGURE 4-15: Comparison of the measured saturation pressures and swelling factors and their predicted values for the $n$-C$_4$H$_{10}$-Lloydminster heavy oil binaries: Feeds #8 and #9
pressures and swelling factors and their predicted values for the \( n-C_4H_{10} \)-Lloydminster heavy oil systems: Feeds #8 and #9. It can be found from FIGURE 4-15 that the saturation pressure increases with the operating temperature for a given feed. As more \( n-C_4H_{10} \) is present in the heavy oil (i.e., a larger \( n-C_4H_{10} \) solubility), the saturation pressure at a given temperature is also increased. This implies that, at the same pressure, the solubility of \( n-C_4H_{10} \) in heavy oil at a higher temperature is smaller than that at a lower temperature, while, at the same temperature, it increases with an increase in pressure. Overall, the measured swelling factor for a given \( n-C_4H_{10} \)-heavy oil system remains almost unchanged at different temperatures. One exception is given to Feed #9 at 396.15 K, for which the measured swelling factor is a little bit lower than the other three data points. The PR EOS together with Equations [4-7] is used to calculate the saturation pressure for Feeds #8 and #9, respectively. The BIPs between \( n-C_4H_{10} \) and heavy oil at different temperatures are calculated via Equation [4-20]. A generally good agreement between the measured and calculated saturation pressures has been achieved, though the accuracy is reduced at temperatures close to the critical temperature of \( n-C_4H_{10} \). An accurate reproduction of the swelling factor of the \( n-C_4H_{10} \)-saturated heavy oil has also been obtained, except that the calculated swelling factor for Feed #9 at 396.15 K shows a relatively large deviation from the measured one.

\( C_3H_8-n-C_4H_{10} \)-Lloydminster heavy oil system: One \( C_3H_8-n-C_4H_{10} \)-Lloydminster heavy oil system is tested in this study. FIGURE 4-16 compares the measured saturation pressures and swelling factors together with their predicted values for the \( C_3H_8-n-C_4H_{10} \)-Lloydminster heavy oil system: Feed #10. It can be found from FIGURE 4-16 that the saturation pressure increases with the operating temperature for the ternary system tested.
FIGURE 4-16: Comparison of the measured saturation pressures and swelling factors and their predicted values for the ternary C₃H₈-\(n\)-C₄H₁₀-Lloydminster heavy oil system: Feed #10
Similar to the CO₂-C₃H₈-heavy oil system, the swelling factor for the C₃H₈-ₙ-C₄H₁₀-Lloydminster heavy oil mixture remains almost unchanged at different temperatures. The saturation pressures for Feed #10 are calculated by using the PR EOS enhanced with the modified alpha function. The BIPs for C₃H₈-heavy oil binary and n-C₄H₁₀-heavy oil binary at different temperatures are predicted via Equations [4-19] and [4-20], respectively. A good agreement exists between the measured and calculated saturation pressures throughout the tested temperature range. A very accurate prediction of the swelling factor of C₃H₈-ₙ-C₄H₁₀-heavy oil mixture is also achieved.

Based on the generally good match between the measured and predicted data on saturation pressures and swelling factors from this work and the previous studies, it is proved that it is an effective and efficient methodology to model the saturation pressures and swelling factors of heavy oil with dissolution of various solvents (i.e., CO₂, C₃H₈ and n-C₄H₁₀) by treating heavy oil sample as a single pseudocomponent and utilizing the generalized BIP correlations developed in this study.

FIGURE 4-17 compares the measured viscosities of C₃H₈-saturated heavy oil by using the capillary viscometer at 298.85 K and predicted ones with different mixing rules. The C₃H₈ dissolution in heavy oil can significantly reduce the heavy oil viscosity (Luo et al., 2007; Badamchi-Zadeh et al., 2009a). For example, the heavy oil viscosity is reduced from 7812.32 cP down to 37.5 cP with dissolution of 14.8 wt% of C₃H₈ (i.e., the corresponding volume fraction of C₃H₈ is 26.1%) at 298.85 K. As can be seen from FIGURE 4-17, the Shu mixing rule, Chung mixing rule and Cragoe mixing rule provide similar prediction accuracies for the C₃H₈-saturated heavy oil viscosities, while the conventional log-type leads to the largest error. The Lobe mixing rule is found to be the
FIGURE 4-17: Measured viscosity and predicted viscosity by using different mixing rules for (a) C$_3$H$_8$-heavy oil mixtures at 298.85 K and (b) n-C$_4$H$_{10}$-heavy oil mixtures at 298.85 K
most accurate one among the mixing rules examined for the given heavy oil sample.

It is very likely to observe asphaltene precipitation at high C$_3$H$_8$ fractions. FIGURE 4-18 shows the precipitated asphaltene particles that are captured on the PVT cell wall for Feed #3 (29.3 wt% C$_3$H$_8$, 70.7 wt% heavy oil) at 1500 kPa and 323.85 K. The digital image is taken after the magnetic mixer is turned off. This implies that the asphaltene precipitation caused by C$_3$H$_8$ dissolution must be taken into account when injecting C$_3$H$_8$ at pressures close to its dew point pressure.

4.4.3. Solvent(s)-CO$_2$-Lloydminster heavy oil systems

PVT tests are also performed to measure the saturation pressures and swelling factors at different temperatures for a C$_3$H$_8$-CO$_2$-Lloydminster heavy oil system with Feed #11 and a n-C$_4$H$_{10}$-CO$_2$-Lloydminster heavy oil system with Feed #12. FIGURE 4-19 illustrates the measured and predicted saturation pressures and swelling factors for these two ternary mixtures at different temperatures. It can be seen from FIGURE 4-19 that, as for a solvent-CO$_2$-heavy oil mixture, the measured saturation pressure increases significantly with the temperature, while the measured swelling factor maintains a high value and only increases slightly with temperature. The BIPs for CO$_2$-heavy oil pair, C$_3$H$_8$-heavy oil pair, n-C$_4$H$_{10}$-heavy oil pair at different temperatures are calculated by using Equations [4-18], [4-19] and [4-20], respectively. Then the calculated BIPs are incorporated into the PR EOS together with Equation [4-7] to predict the saturation pressures and swelling factors for the two ternary mixtures. As can also be observed from FIGURE 4-19, there exists a generally good agreement between the measured and predicted saturation pressures and swelling factors. The viscosity of the ternary C$_3$H$_8$-
FIGURE 4-18: Asphaltene precipitation observed on the PVT cell wall for Feed #3 (29.3 wt% C₃H₈, 70.7 wt% heavy oil) at 1500.0 kPa and 323.85 K
FIGURE 4-19: Measured and predicted saturation pressures and swelling factors for the C$_3$H$_8$-CO$_2$-heavy oil system with Feed #11 (10.3 wt% C$_3$H$_8$, 11.0 wt% CO$_2$, 78.7 wt% Lloydminster heavy oil) and the n-C$_4$H$_{10}$-CO$_2$-heavy oil system with Feed #12 (10.1 wt% n-C$_4$H$_{10}$, 7.1 wt% CO$_2$, 82.8 wt% Lloydminster heavy oil)
CO₂-Lloydminster heavy oil mixture at 318.75 K and saturation pressure of 6657.0 kPa is measured to be 12.1 cP, while the viscosity of the ternary \textit{n-C}_4\textit{H}_{10}-\textit{CO}_2-\textit{Lloydminster}
heavy oil mixture at 298.85 K and saturation pressure of 3154.0 kPa is measured to be 34.4 cP.

In order to examine the effect of adding a solvent into CO₂ stream on the swelling factor and viscosity of CO₂-heavy oil system, the swelling factor of CO₂-saturated heavy oil at 298.85 K is calculated by using the PR EOS together with Equations [4-7] and [4-18] and by using a swelling factor correlation (Emera and Sarma 2008), respectively, while the viscosity of CO₂-saturated heavy oil at 298.85 K is calculated with a viscosity correlation (Emera and Sarma 2008) (See FIGURE 4-20). In addition to the predicted swelling factors and mixture viscosity for the CO₂-Lloydminster heavy oil system at 298.85 K, FIGURE 4-20 also presents the swelling factor of the ternary C₃H₈-CO₂-Lloydminster heavy oil mixture measured at 298.85 K and saturation pressure of 4642.0 kPa together with the swelling factor and viscosity of the \textit{n-C}_4\textit{H}_{10}-\textit{CO}_2-\textit{Lloydminster}
heavy oil mixture measured at 298.85 K and saturation pressure of 3154.0 kPa.

By comparing FIGUREs 4-13 and 4-20, it can be found that, at the same saturation pressure, C₃H₈ is able to swell the heavy oil to a far larger degree than pure CO₂. Similarly, \textit{n-C}_4\textit{H}_{10} can swell heavy oil to a larger degree than pure CO₂ (Li and Yang 2012). This is mainly attributed to two aspects: 1) Solubility of C₃H₈ or \textit{n-C}_4\textit{H}_{10} in heavy oil is much higher than CO₂ under the same pressure; and 2) Density of liquid C₃H₈ or \textit{n-C}_4\textit{H}_{10} is smaller than that of liquid CO₂. As can be seen from FIGURE 4-20, at the same saturation pressure and temperature, addition of \textit{n-C}_4\textit{H}_{10} into CO₂ stream increases the swelling factor from 1.06 to 1.37, but decreases the viscosity from 426.9 cP to 34.4 cP.
FIGURE 4-20: Predicted swelling factor and mixture viscosity for the CO$_2$-Lloydminster heavy oil system at 298.85 K, respectively. The swelling factor is predicted by using the PR EOS together with Equations [4-7] and [4-18] as well as a genetic algorithm-based swelling factor correlation (Emera and Sarma 2008), respectively, while the viscosity is calculated with a genetic algorithm-based viscosity correlation (Emera and Sarma 2008)
FIGURE 4-20 also shows that, at the same saturation pressure and temperature, a significantly larger swelling factor of 1.47 can be achieved by adding C\textsubscript{3}H\textsubscript{8} into CO\textsubscript{2} stream compared to that of 1.10 for the CO\textsubscript{2}-heavy oil system. The enhanced swelling factor and viscosity reduction effect is achieved mainly through the enhanced dissolution of the alkane solvent either C\textsubscript{3}H\textsubscript{8} or \textit{n}-C\textsubscript{4}H\textsubscript{10} into heavy oil.

4.4.4. Formation of foamy heavy oil

One interesting phenomenon is observed during all the PVT experiments for solvent(s)-CO\textsubscript{2}-heavy oil systems. Foamy solvent-heavy oil mixture has been observed when the mixture is subjected to a sudden pressure decrease and released to the atmosphere. The foamy oil behaviour is a beneficial mechanism for the practical implementation of solvent-based processes for heavy oil recovery. FIGURE 4-21 illustrates a sequence of images of the C\textsubscript{3}H\textsubscript{8}-\textit{n}-C\textsubscript{4}H\textsubscript{10}-heavy oil mixture which is released to the atmosphere from the PVT cell at saturation pressure and 298.85 K right after the viscosity measurements. The five digital images are taken in sequence when the mixture is released at 0 s, 30 s, 60 s, 90 s, and 120 s, respectively. It is observed from FIGURE 4-21 that the discharge process is terminated within a short time period of about 120 s. A subsequent check on the tubing and PVT cell shows that there is only little heavy oil or solvents remaining in the tubing and PVT cell. The high mobility and efficient self-cleaning phenomenon of the foamy heavy oil are mainly attributed to two aspects. Firstly, the emergence of gas bubbles in the heavy oil due to sudden pressure decrease acts as an efficient solution-gas-drive mechanism inside the tubing (Turta \textit{et al.}, 2003; Kumar and Mahadevan, 2012). Secondly, C\textsubscript{3}H\textsubscript{8}-\textit{n}-C\textsubscript{4}H\textsubscript{10} mixture in heavy oil is fairly soluble in
FIGURE 4-21: Sequential images of the foamy C₃H₈-\textit{n}-C₄H₁₀-heavy oil system Feed #10 which is released to atmosphere from the PVT cell at saturation pressure and 298.85 K after the viscosity measurements at: (a) 0 s; (b) 30 s; (c) 60 s; (d) 90 s; and (e) 120 s. The total volume of the ternary mixture discharged is around 10 cm³ at saturation conditions.
heavy oil at atmospheric pressure. This means that the heavy oil is still able to preserve a low viscosity level even at atmospheric pressure, which facilitates swelling the heavy oil and carrying it by the gas solvents.

4.5 Summary

Techniques have been developed to experimentally and theoretically examine the enhanced swelling effect and viscosity reduction of CO₂-saturated heavy oil with addition of either C₃H₈ or n-C₄H₁₀. The newly developed three BIP correlations CO₂-heavy oil binaries, C₃H₈-heavy oil binaries and n-C₄H₁₀-heavy oil binaries in PR EOS together with Equation [4-7] are able to reproduce the experimental solubility data and predict the swelling factor with a good accuracy. The proposed BIP correlations are also validated with the recently published phase behaviour data, including saturation pressures and L₁L₂V three phase boundaries, for CO₂-C₃H₈-heavy oil systems. A good agreement between the experimental and calculated phase behaviour data is obtained.

PVT measurements on the saturation pressure, swelling factor and viscosity of the solvent(s)-CO₂-heavy oil system indicate that, under the same conditions, a significantly increased swelling effect of heavy oil can be obtained by adding either C₃H₈ or n-C₄H₁₀ into CO₂ stream. An enhanced viscosity reduction of the CO₂-heavy oil system can be also achieved in the presence of either C₃H₈ or n-C₄H₁₀. The enhanced swelling effect and viscosity reduction caused by adding either C₃H₈ or n-C₄H₁₀ into CO₂ stream implies that solvent(s)-enriched CO₂ flooding is a highly promising technique to recover heavy oil resources where other recovery techniques are not economically or efficiently available. The PR EOS together with the proposed BIP correlations is able to predict the
saturation pressures and swelling factors of solvent(s)-CO₂-heavy oil systems with a good accuracy. In addition, the Lobe’s mixing rule is found to be generally superior to other mixing rules in evaluating solvent-saturated heavy oil viscosities.
5.1 Introduction

Immiscible CO₂ flooding is a non-thermal recovery method that has considerable potential for a large range of heavy oil reservoirs, where other enhanced oil recovery (EOR) techniques are not applicable (Tuzunoglu and Bagci, 2000). During the immiscible flooding process, CO₂ is injected into the formation to highly mobilize the contacted oil and displace it towards the production well once diluted and swollen. Oil mobility is improved due to solubility of CO₂ in the oil that causes both a reduction in the viscosity and an increase in oil volume (Al-Abri and Amin, 2010). Recovery mechanisms related to immiscible CO₂ flooding consist of viscosity reduction, oil swelling effect, IFT reduction, and blowdown recovery (Rojas and Farouq Ali, 1986). The dissolved CO₂ functions as a surface-active agent, which is responsible for the IFT reduction (Yang and Gu, 2006). Addition of rich solvents, such as C₃H₈ and/or n-C₄H₁₀, into CO₂ stream is a promising technique that can improve the performance of immiscible CO₂ processes in heavy oil reservoirs.

Experiments are first carried out, in this study, to examine the IFT reduction effect of CO₂-heavy oil system caused by addition of C₃H₈ and/or n-C₄H₁₀, which has not been covered previously. Due to the large uncertainty involved in characterization of heavy oils, it is extremely difficult to accurately model the equilibrium IFT for the solvent(s)-CO₂-heavy oil systems. In this study, a recently proposed mechanistic parachor model (Ayirala and Rao, 2006) is used to model the equilibrium IFT of solvent(s)-CO₂-heavy oil...
systems. More specifically, the PR EOS (Peng and Robinson, 1976) together with the
new alpha function Equation [4-7] is used to perform two-phase flash calculations. The
flash calculation results are then used as inputs for the mechanistic parachor model
(Ayirala and Rao, 2006). Both the parachor of the heavy oil and the mass transfer
exponent in mechanistic parachor model are treated as two tuning parameters and
optimized by minimizing the discrepancy between the measured and calculated
equilibrium IFTs.

5.2 Experimental

An axisymmetric drop shape analysis (ADSA) system (Yang et al., 2005) has been
used to measure both the dynamic and equilibrium IFTs between the heavy oil and pure
solvents (i.e., CO₂, C₃H₈, and n-C₄H₁₀) together with their mixtures (i.e., CO₂-C₃H₈, CO₂-
n-C₄H₁₀, C₃H₈-n-C₄H₁₀ and CO₂-C₃H₈-n-C₄H₁₀).

5.2.1. Materials

The heavy oil sample is collected from the Lloydminster area in Saskatchewan,
Canada. The molar mass of the Lloydminster heavy oil is measured to be 482 g/mol with
a freezing point depression method. The density of the Lloydminster heavy oil at 60°F is
measured to be 999.7 kg/m³ by using a densitometer (DMA512P, Anton Paar, USA). The
compositional analysis results of the Lloydminster heavy oil are obtained by using the
simulated distillation method and provided in TABLE 4-1.

The gas solvents, CO₂, C₃H₈, and n-C₄H₁₀ (Praxair, Canada) used in the IFT
measurements have purities of 99.998 mol%, 99.99 wt%, and 99.9 wt%, respectively.
The pure gases are also used to prepare seven gas mixtures for the IFT measurements. The seven gas mixtures are listed in TABLE 5-1.

5.2.2. IFT measurements

In this study, the axisymmetric drop shape analysis (ADSA) for the pendant drop case is employed to measure both the dynamic and equilibrium IFTs of the aforementioned three pure solvents and seven solvent mixtures with the Lloydminster heavy oil at different temperatures and pressures.

FIGURE 5-1 shows a schematic of the ADSA system for the pendant drop case used in this study. A major component of this system is a see-through-windowed high-pressure cell (IFT-10, Temco), which has a chamber volume of 41.5 cm³. The maximum operating pressure and temperature of this pressure cell are 69000 kPa and 177.0°C, respectively. The temperature during the measurements is maintained by a heating tape (HT95504×1, Electrothermal) with the accuracy of ±0.1°C, which is connected to a stepless temperature controller (CN45515, Thermolyne). The pressure of the high-pressure cell is measured with a digital precision test gauge (Model 2089, Ashcroft) with an accuracy of 0.05% of full range, while the temperature is measured by using a thermocouple (JMQSS-125U-6, Omega) with an accuracy of 0.1°C. The light source and glass diffuser are used to provide a uniform illumination for the pendant oil drop. A MZ6 microscope camera (Leica, Germany) is used to capture the sequential digital images of the dynamic pendant drops. The entire experimental setup is positioned on a vibration-free table (RS4000, Newport). All the digital images of the pendant oil drop are stored in a desktop computer, subsequently digitized and computed.
TABLE 5-1: Compositions of seven solvent mixtures

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>89.3 mol% CO₂, 10.7 mol% C₃H₈</td>
</tr>
<tr>
<td>2</td>
<td>76.0 mol% CO₂, 24.0 mol% C₃H₈</td>
</tr>
<tr>
<td>3</td>
<td>62.3 mol% CO₂, 37.7 mol% C₃H₈</td>
</tr>
<tr>
<td>4</td>
<td>81.5 mol% CO₂, 18.5 mol% n-C₄H₁₀</td>
</tr>
<tr>
<td>5</td>
<td>76.8 mol% C₃H₈, 23.2 mol% n-C₄H₁₀</td>
</tr>
<tr>
<td>6</td>
<td>61.4 mol% C₃H₈, 38.6 mol% n-C₄H₁₀</td>
</tr>
<tr>
<td>7</td>
<td>93.0 mol% CO₂, 5.9 mol% C₃H₈, 1.1 mol% n-C₄H₁₀</td>
</tr>
</tbody>
</table>
FIGURE 5-1: Schematic diagram of experimental setup for measuring the dynamic and equilibrium IFT of solvent(s)-CO₂-heavy oil systems by using the ADSA technique for the pendant drop case
The three gaseous solvents (CO$_2$, C$_3$H$_8$, and n-C$_4$H$_{10}$) are pressurized in three sample cylinders which are controlled by using a manual positive displacement pump (PMP-500-1-10-HB, DBR, Canada). The heavy oil sample is contained in a sample cylinder that is controlled by a syringe pump (500HP, ISCO Inc., USA). The IFT of the CO$_2$-heavy oil system is measured in the pressure ranges of 1101-15640 kPa at 21.0°C and 3190-11175 kPa at 44.0°C, respectively, C$_3$H$_8$-heavy oil system in the pressure ranges of 195-801 kPa at 21.0°C and 201-823 kPa at 46.1°C, respectively, and n-C$_4$H$_{10}$-heavy oil system in the pressure ranges of 123-213 kPa at 21.0°C and 116-219 kPa at 48.6°C, respectively. It should be noted that the dynamic and equilibrium IFTs of the solvent mixture-heavy oils systems are all measured below the dewpoint pressures of the respective solvent mixtures at 21.0°C.

Prior to each measurement between pure gas solvent and heavy oil, the high-pressure cell is thoroughly cleaned with ethanol and then flushed with the pure solvent. Then the pressure cell is filled with a pure gas solvent at a specified pressure and a constant temperature. As for the IFT measurements for a solvent mixture, one solvent is first injected into the pressure cell to pressurize the pressure cell to a certain pressure. Subsequently, another solvent is then injected into the pressure cell, resulting in a different pressure, until all the desired solvents are present in the pressure cell with their individual fraction. A sampler (Swagelok, Canada) with a volume of 10 cm$^3$ and a pressure rating of 1000 psi is used to collect the gas solvent sample inside the high pressure cell. Then the composition of the sample is determined by using a gas chromatography (GC) method. After the pressure and temperature inside the pressure cell are stabilized, the heavy oil is introduced from the sample cylinder to the pressure cell to
form a pendant oil drop at the syringe needle tip. Once a well-shaped pendant drop is formed, the sequential digital images of the dynamic pendant oil drop at different times are acquired and stored automatically in the desktop computer. It should be noted that the density of heavy oil and density of bulk gas phase are required inputs for implementing the ADSA program. In this study, the density of Lloydminster heavy oil at any temperature and pressure can be calculated by using the heavy oil density correlation presented elsewhere (Li et al., 2011), while the density of the bulk solvent phase is calculated with the PR EOS. Thereafter, the ADSA program for the pendant drop case is executed to determine both the dynamic and equilibrium IFT by solving the Laplace equation of capillarity. Each IFT measurement is repeated three times to ensure the repeatability of the measurement.

5.3 Mathematical Formulation

5.3.1. PR EOS model

The PR EOS is chosen as the equation of state for describing phase behaviour of solvent(s)-CO₂-heavy oil systems. The detailed expressions of the PR EOS together with the new alpha function can be found in CHAPTER 3 of this dissertation. In this study, the heavy oil sample is treated as a single pseudocomponent, while the specific gravity and molar mass are used as the two characterization parameters. The characterization method for the heavy oil sample is provided in CHAPTER 4. Once the heavy oil is characterized by its critical properties, the BIP matrix (δ) remains the single parameter that is needed in PR EOS to model the phase behaviour of solvent(s)-CO₂-heavy oil systems at a given condition. The BIP matrix for a four-component fluid system which is comprised of CO₂,
C₃H₈, n-C₄H₁₀ and heavy oil is shown in TABLE 4-6. The fixed δ₁₂ and δ₁₃ values for CO₂-C₃H₈ and CO₂-n-C₄H₁₀ are rigorously reviewed data which are retrieved from a commercial phase behaviour simulator (Computer Modelling Group Ltd., 2009), while δ₂₃ value for C₃H₈-n-C₄H₁₀ is calculated to be 0.00087 by using the commonly used correlation for hydrocarbon-hydrocarbon binaries (Computer Modelling Group Ltd., 2009),

\[
\delta_\gamma = 1 - \left[ \frac{2\sqrt[3]{V_{c{i}}^{1/3}V_{q{j}}^{1/3}}}{V_{c{i}}^{1/3} + V_{q{j}}^{1/3}} \right]^{1.2} \quad [5-1]
\]

Correlations for δ₁₄ and δ₂₄ have been developed by fitting experimental solubility data for CO₂-heavy oil systems and C₃H₈-heavy oil systems that are presented in CHAPTER 4 (See Equations [4-18] and [4-19]), respectively. The BIP between n-C₄H₁₀ and the Lloydminster heavy oil is estimated by Equation [5-1].

5.3.2. Mechanistic parachor model for equilibrium IFT

Parachor model is a conventional IFT model that is widely used in petroleum industry for calculating IFT between two immiscible fluid systems. Macleod (1923) and Sudgen (1924) related surface tension of a pure compound to the molar density difference between the coexisting phases with,

\[
\sigma^{1/4} = P_a \left( \rho^l - \rho^v \right) \quad [5-2]
\]

where σ is surface tension (mN/m), \( \rho^l \) and \( \rho^v \) are molar densities of the liquid and vapour phases (mol/cm³), respectively, and \( P_a \) is known as the parachor.
The original parachor model for pure substances was extended to a multicomponent mixture by Weinaug and Katz (1943) as follows,

\[ \gamma^{1/4} = \rho^1 \sum_{i=1}^{nc} x_i P_{ai} - \rho^v \sum_{i=1}^{nc} y_i P_{ai} \]  \[5-3\]

where \( \gamma \) is equilibrium IFT between the bulk liquid phase and vapour phase of the multicomponent mixture, \( x_i \) and \( y_i \) are mole percentages of the \( i \)th component in the bulk liquid phase and vapour phase, respectively, \( nc \) is number of components in the mixture, and \( P_{ai} \) is parachor of the \( i \)th component. Although many parachor correlations have been proposed to estimate the parachor of petroleum fraction (Firoozabadi et al., 1988; Ahmed, 1989), there is no consensus on which correlation provides the most accurate estimation for heavy oil. In this study, the parachor of the Lloydminster heavy oil \( P_{ao} \) is treated as a tuning parameter in the parachor model.

The parachor model has found its successful application for predicting IFT of pure compounds and binary mixtures. However, this model provides a poor accuracy for predicting IFT of complex hydrocarbon mixtures, in particular, the ones involved with heavy oils. Ayirala and Rao (2006) recently proposed a mechanistic parachor model that took into account of mass transfer effect by introducing a ratio of diffusivity coefficients raised to an exponent. The mechanistic parachor model is given as (Ayirala and Rao, 2006),

\[ \gamma^{1/4} = \left( \frac{D_{os}}{D_{so}} \right)^{n/4} \left( \rho^1 \sum_{i=1}^{nc} x_i P_{ai} - \rho^v \sum_{i=1}^{nc} y_i P_{ai} \right) \]  \[5-4\]

where \( D_{os} \) is diffusivity of oil in gas solvent, \( D_{so} \) is diffusivity of gas solvent in oil, and \( n \) denotes the exponent whose sign and value characterize the type and extent of the
governing mass transfer mechanism for fluid phase equilibria. As noted by Ayirala and Rao (2006), if \( n > 0 \), vaporization of lighter components from the oil into the gas phase plays a dominant role in the governing mass transfer mechanism, whereas, if \( n < 0 \), condensation of gas solvents into oil contributes more. A value of \( n \) equal to approximately zero indicates equal proportions of vaporizing and condensing mass transfer mechanisms. The empirical diffusivity correlation provided by Wilke and Chang (1995) is used to estimate the diffusivities in Equation [5-4],

\[
D_{AB} = \frac{117.3 \times 10^{-18} (kM_B)^{0.5} T}{\mu^{0.6}}
\]  

[5-5]

where \( D_{AB} \) is diffusivity of solute A in solvent B (m²/s), \( M_B \) is molar mass of the solvent B (g/mol), \( T \) is temperature (K), \( \mu \) is solution viscosity (Pa·s), \( V_A \) is solute molar volume at normal boiling point (m³/kmol), and \( k \) is association factor for solvent, which is equal to unity for unassociated solvents. The substances considered in this study, i.e., CO₂, C₃H₈, \( n \)-C₄H₁₀, and heavy oil, are assumed to be unassociated, resulting in \( k = 1 \). Equation [5-5] is extended to multicomponent mixtures by using (Ayirala and Rao, 2006),

\[
M_B = \sum_{i=1}^{nc} x_{Bi} M_{Bi}
\]  

[5-6]

\[
V_A = \sum_{i=1}^{nc} x_{Ai} V_{Ai}
\]  

[5-7]

where \( x_{Bi} \) is mole fraction of the \( i \)th component in the mixture, \( M_{Bi} \) is molar mass of the \( i \)th component, and \( V_{Ai} \) is molar volume of \( i \)th component at normal boiling point. In this study, the molar volumes of CO₂, C₃H₈, \( n \)-C₄H₁₀, and heavy oil at normal boiling point are calculated with the accurate Rackett equation of Spencer and Danner (1972),
\[ V_A = \frac{RT_c}{P_c} Z_{RA}^{1+[(1-T_{br})^{1/7]}} \]  

[5-8]

where \( T_{br} \) is the reduced temperature at normal boiling point, and \( Z_{RA} \) is Rackett parameter that is a constant for a given substance. The Rackett parameter of the heavy oil sample can be calculated with Equation [4-13], while the following correlation for the PR EOS is used to correct molar volume for pure substance (Twu and Chan, 2009),

\[ C = 0.406501 \left( \frac{RT_c}{P_c} \right) (0.260484 - Z_{RA}) \]  

[5-9]

Once all the required input information for the mechanistic parachor model has been acquired, the parachor of the Lloydminster heavy oil and the exponent \( n \) in Equation [5-4] are optimized by minimizing the root-mean-squared relative error (RMSRE) between the measured and calculated IFT data,

\[ RMSRE_{IFT} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left( \frac{IFT_{i}^{\text{cal}} - IFT_{i}^{\text{exp}}} {IFT_{i}^{\text{exp}}} \right)^2} = f(n, P_{ao}) \]  

[5-10]

where \( IFT_{i}^{\text{cal}} \) is the calculated IFT, \( IFT_{i}^{\text{exp}} \) is the measured IFT, and \( N \) is total number of data point.

5.4 Results and Discussion

5.4.1. Dynamic IFT of the solvent(s)-CO\(_2\)-heavy oil systems

The dynamic IFT of solvent(s)-heavy oil systems are measured as a function of time to examine the effect of mass transfer between solvent(s) and heavy oil on IFT. FIGURE 5-2 plots four typical measurements of dynamic IFT for three pure solvents (CO\(_2\), C\(_3\)H\(_8\), and \(n\)-C\(_4\)H\(_{10}\)) and a solvent mixture (62.3 mol\% CO\(_2\), 37.7 mol\% C\(_3\)H\(_8\)) at 21.0°C. It can
be seen from Figure 5-2 that, for the CO₂-heavy oil system, the dynamic IFT remains almost constant as a function of time at \( P = 1100 \) kPa and \( T = 21.0^\circ\text{C} \). This means that the CO₂-heavy oil interface is able to quickly reach the equilibrium state, even though the dissolution process of CO₂ into the pendant heavy oil drop may take place for a long duration (Yang and Gu, 2005; 2006). As for the C₃H₈-heavy oil system at 195 kPa and 21.0°C and \( n\)-C₄H₁₀-heavy oil system at 215 kPa and 21.0°C, the dynamic IFT varies with a slightly larger degree at the initial stage of the mass transfer process compared to that of the CO₂-heavy oil system and remains almost a constant afterwards. The relatively large variation of the dynamic IFT for the C₃H₈-heavy oil and \( n\)-C₄H₁₀-heavy oil systems may be attributed to the fast and large swelling of the pendant heavy oil drop due to the dissolution of rich solvents (Yang and Gu, 2005).

The variation trend of the measured dynamic IFTs for the pure solvent-heavy oil systems are in a good agreement with those reported previously (Yang and Gu, 2005). For the solvent mixture (62.3 mol% CO₂, 37.7 mol% C₃H₈) and heavy oil system at 1600 kPa and 21.0°C, the measured dynamic IFTs fluctuate around 15 mN/m during the observation period. This may be due to the interplay of mass transfer processes of the three solvents present in the mixture into the pendant heavy oil drop. Overall, it is reasonable to consider that the dynamic IFT can reach its equilibrium value within a short period (600 s).
FIGURE 5-2: Measured dynamic IFT as a function of time between various solvents and heavy oil at 21.0°C
5.4.2. Equilibrium IFT of the solvent(s)-CO\(_2\)-heavy oil systems

In order to examine the effect of adding rich solvent(s) C\(_3\)H\(_8\) and \(n\)-C\(_4\)H\(_{10}\) into CO\(_2\) stream on the equilibrium IFT, the equilibrium IFT measurements have been also conducted between the Lloydminster heavy oil and seven solvent mixtures that are composed of CO\(_2\), C\(_3\)H\(_8\), and \(n\)-C\(_4\)H\(_{10}\) with varied fractions. All the equilibrium IFTs of solvent(s)-heavy oil systems are measured in the liquid-vapour phase region, except for the CO\(_2\)-heavy oil system. The conventional parachor model is found to significantly underestimate the measured equilibrium IFTs of the solvent(s)-heavy oil systems in the liquid-liquid or dense fluid-liquid (at supercritical conditions) phase region, though it can represent qualitatively the measured equilibrium IFTs of the solvent(s)-CO\(_2\)-heavy oil systems in the liquid-vapour phase region. Therefore, only the equilibrium IFT data for all the solvent(s)-CO\(_2\)-heavy oil systems measured in the liquid-vapour phase region are selected to optimize the parachor of Lloydminster heavy oil and mass transfer exponent in the mechanistic parachor model. TABLE 5-2 shows the basic physical properties of the solvents and Lloydminster heavy oil used in the mechanistic parachor model. The BIPs for CO\(_2\)-heavy oil pair and C\(_3\)H\(_8\)-heavy oil pair are predicted by using Equations [4-18] and [4-19], respectively, while BIP for \(n\)-C\(_4\)H\(_{10}\)-heavy oil pair is calculated with Equation [5-1].

FIGURE 5-3 shows variation of the objective function \(RMSRE_{IFT}\) with the parachor of Lloydminster heavy oil and the mass transfer exponent in the mechanistic model. The optimum parachor of Lloydminster heavy oil and mass transfer exponent are found to be 835 and -0.448, respectively, which leads to the minimum \(RMSRE_{IFT}\) of 0.1574. Hence,
TABLE 5-2: Physical properties of the three solvents and Lloydminster heavy oil used in the mechanistic parachor model

<table>
<thead>
<tr>
<th>Component</th>
<th>$P_C$, kPa</th>
<th>$T_C$, K</th>
<th>$\omega$</th>
<th>$Z_{ra}$</th>
<th>$V_\omega$, m$^3$/kmol</th>
<th>$V_A$, m$^3$/kmol</th>
<th>Parachor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>7378</td>
<td>304.14</td>
<td>0.2238</td>
<td>0.2736</td>
<td>0.0940</td>
<td>0.0356</td>
<td>78.0</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>4246</td>
<td>369.80</td>
<td>0.1520</td>
<td>0.2763</td>
<td>0.2030</td>
<td>0.0757</td>
<td>150.0</td>
</tr>
<tr>
<td>$n$-C$<em>4$H$</em>{10}$</td>
<td>3786</td>
<td>425.20</td>
<td>0.1930</td>
<td>0.2728</td>
<td>0.2550</td>
<td>0.0967</td>
<td>189.9</td>
</tr>
<tr>
<td>Lloydminster heavy oil</td>
<td>1265</td>
<td>933.66</td>
<td>1.0288</td>
<td>0.2622</td>
<td>1.2460</td>
<td>0.6962</td>
<td>$P_{ao}$</td>
</tr>
</tbody>
</table>
FIGURE 5-3: Variation of the objective function $RMSRE_{IFT}$ with the parachor of Lloydminster heavy oil $P_{ao}$ and the mass transfer exponent $n$ in the mechanistic model
the mechanistic parachor model for describing the equilibrium IFT of solvent(s)-CO\(_2\)-heavy oil systems is finalized as follows,

\[
\gamma = \left( \frac{D_{ax}}{D_{so}} \right)^{-0.448} \left( \rho^4 \sum_{i=1}^{nc} x_i P_{ai} - \rho^\gamma \sum_{i=1}^{nc} y_i P_{ai} \right)^4
\]  \[5-11\]

Equation [5-11] results in a percentage average absolute deviation (%AAD) of 11.86% for reproducing the measured 56 liquid-vapour equilibrium IFT data points. It is worthwhile mentioning that the negativity of exponent \(n\) indicates that the condensation or dissolution of gas solvents into heavy oil is the controlling mass transfer process for the solvent(s)-heavy oil systems (Ayirala and Rao, 2006). It is reasonable to consider the fact that the Lloydminster heavy oil is mainly composed of heavy hydrocarbon components, and thus the extraction of light components from heavy oil by solvent(s) would be insignificant. This can be also confirmed by the calculated phase compositions. For example, for Mixture #7 (93.0 mol% CO\(_2\), 5.9 mol% C\(_3\)H\(_8\), 1.1 mol% \(n\)-C\(_4\)H\(_{10}\)), the calculated phase compositions for the feed (92.9 mol% CO\(_2\), 5.9 mol% C\(_3\)H\(_8\), 1.1 mol% \(n\)-C\(_4\)H\(_{10}\), 0.1 mol% heavy oil) at 1101 kPa and 21.0°C are (14.0 mol% CO\(_2\), 4.9 mol% C\(_3\)H\(_8\), 2.8 mol% \(n\)-C\(_4\)H\(_{10}\), 78.3 mol% heavy oil) for the liquid phase and (93.0 mol% CO\(_2\), 5.9 mol% C\(_3\)H\(_8\), 1.1 mol% \(n\)-C\(_4\)H\(_{10}\), 0.0 mol% heavy oil) for the gas phase. It is apparent from the calculated phase compositions that the gas solvents CO\(_2\), C\(_3\)H\(_8\) and \(n\)-C\(_4\)H\(_{10}\) dissolve into heavy oil, while heavy oil is not noticeable in the gas phase. It is also valid for other solvents-CO\(_2\)-heavy oil systems where no heavy oil or only negligible trace of heavy oil is present in the gas phase.

**Pure solvent-heavy oil system:** FIGURE 5-4a depicts the measured and calculated equilibrium IFTs for the CO\(_2\)-heavy oil system at 21.0°C and 44.0°C, respectively. In
FIGURE 5-4: Comparison of the measured and calculated equilibrium IFT using the mechanistic model Equation [5-11] for the pure solvent-heavy oil systems: (a) CO₂-heavy oil system at 21.0°C and 44.0°C, respectively; (b) C₃H₈-heavy oil system at 21.0°C and 46.1°C, respectively; and (c) n-C₄H₁₀-heavy oil system at 21.0°C and 48.6°C, respectively.
general, at a given temperature, it can be seen from FIGURE 5-4a that the equilibrium IFT of the CO$_2$-heavy oil system decreases significantly at the initial stage as pressure increases and then decreases slightly with the further increase of pressure. In addition, the IFT of the CO$_2$-heavy oil system at 44.0°C is found to be higher than that at 21.0°C. The similar variation trend of IFT with pressure and temperature has also been reported for a CO$_2$-light oil system (Yang and Gu, 2005). The variation trend of IFT with pressure and temperature is consistent with the change of CO$_2$ solubility with pressure and temperature. The CO$_2$ solubility at a higher temperature is lower than that at a lower temperature, resulting in a higher IFT (Simon and Graue, 1965).

At a given temperature, the initial dramatic reduction of IFT is mainly because of the increased solubility of CO$_2$ in heavy oil due to an increase in pressure (Simon and Graue, 1965). At some points where liquid-liquid two phase (subcritical for CO$_2$) or dense fluid-liquid (supercritical for CO$_2$) two phase appears, further increase of pressure will only lead to a slight increase of CO$_2$ solubility in heavy oil (Sayegh et al., 1990), consequently, leading to only a slight decrease of the IFT. It is found that the transition pressure where the large IFT reduction terminates due to pressure increase can be approximated with the vapour pressure of CO$_2$ at subcritical temperatures or extrapolated vapour pressure of CO$_2$ at supercritical temperatures. The transition pressures for the CO$_2$-heavy oil system at 21.0°C (subcritical) and 44.0°C (supercritical) are estimated to be 5875 kPa and 9760 kPa (See FIGURE 5-4a), respectively. The calculated IFTs for the CO$_2$-heavy oil system by using the mechanistic model and the phase densities are also plotted in FIGURE 5-4a.

It can be seen that the mechanistic parachor model provides a qualitative agreement with the measured IFTs for the CO$_2$-heavy oil system at pressures lower than the
aforementioned transition pressure, but significantly underestimates the IFT at pressures beyond the transition pressure. At a higher pressure, the CO2-dominant phase exists as either a liquid at subcritical temperatures (e.g., 21.0°C) or a liquid-like dense fluid at supercritical temperatures (e.g., 44.0°C). It can be found from FIGURE 5-4 the parachor model provides low IFTs for the liquid-liquid region or dense fluid-liquid region. This is partially attributed to a smaller density difference of the coexisting liquid phases as shown in FIGURE 5-4a compared to that of the liquid and vapour phase (See Equation [5-11]). In addition, it is the discontinuity of vapour phase density that causes the discontinuous change in the calculated IFT at 21.0°C.

FIGURE 5-5 shows the calculated P-X diagrams for CO2-heavy oil system by using PR EOS with the modified alpha function at 21.0°C and at 44.0°C, respectively. It can be seen from FIGURE 5-4a that the transition pressure where the discontinuity of IFT data occurs at 21°C coincides with the L1L2V three-phase coexisting pressure, i.e., the vapour pressure of CO2 in this case. FIGUREs 5-4b and c show the measured and calculated equilibrium IFT for the C3H8-heavy oil system at 21.0°C and 46.1°C, and n-C4H10-heavy oil system at 21.0°C and 48.6°C, respectively. Comparison of FIGUREs 5-4a, b and c shows that, at the same temperature and pressure, n-C4H10 leads to the lowest IFT, while CO2 has the highest IFT. This is because n-C4H10 has the highest solubility in heavy oil, whereas CO2 has the lowest solubility in heavy oil at the same temperature and pressure (Yang and Gu, 2006). It should be noted in FIGURE 5-4c that the mechanistic parachor model leads to a fairly underestimated equilibrium IFT for the n-C4H10-heavy oil system.

**Solvent(s)-CO2-heavy oil system:** FIGURE 5-6 compares the measured and calculated equilibrium IFTs for the CO2-heavy oil system, CO2-C3H8-heavy oil system,
FIGURE 5-5: Calculated $P$-$X$ diagrams for CO$_2$-heavy oil system by using PR EOS with the modified alpha function: (a) at 21.0°C and (b) at 44.0°C, respectively.
FIGURE 5-6: Comparison of the measured and calculated equilibrium IFT using Equation [5-11] for the CO₂-heavy oil system, CO₂-C₃H₈-heavy oil system (i.e., Mixtures #1, #2 and #3), and C₃H₈-heavy oil system at 21.0°C, respectively. The compositions of Mixtures #1, #2 and #3 are (89.3 mol% CO₂, 10.7 mol% C₃H₈), (76.0 mol% CO₂, 24.0 mol% C₃H₈), and (62.3 mol% CO₂, 37.7 mol% C₃H₈), respectively.
and \(\text{C}_3\text{H}_8\)-heavy oil system at 21.0°C, respectively. It is interesting to find from FIGURE 5-6 that addition of \(\text{C}_3\text{H}_8\) into CO\(_2\) stream is able to significantly reduce the IFT between CO\(_2\) and heavy oil. For example, the IFT of the CO\(_2\)-heavy oil system at 3101 kPa and 21.0°C is reduced from 19.92 mN/m to 10.18 mN/m by adding 24.0 mol% \(\text{C}_3\text{H}_8\) into the CO\(_2\) stream. A greater reduction of IFT is achieved with a larger mole fraction of \(\text{C}_3\text{H}_8\) that is present in the CO\(_2\)-\(\text{C}_3\text{H}_8\) mixture.

The IFT reduction effect caused by addition of \(\text{C}_3\text{H}_8\) can be mainly attributed to two factors. Firstly, the addition of \(\text{C}_3\text{H}_8\) into the CO\(_2\) increased the solubility of gas solvents in the heavy oil. Secondly, the parachor difference between \(\text{C}_3\text{H}_8\) and heavy oil is smaller than that between CO\(_2\) and heavy oil, which tends to result in a lower IFT according to Equation [5-16]. The mechanistic parachor model provides a reasonably accurate prediction of the IFT for the CO\(_2\)-\(\text{C}_3\text{H}_8\)-heavy oil systems.

The measured and calculated equilibrium IFTs for the CO\(_2\)-\(n\)-\(\text{C}_4\text{H}_{10}\)-heavy oil system are shown in FIGURE 5-7. As can be seen from FIGURE 5-7, a significant reduction of IFT can be achieved by adding \(n\)-\(\text{C}_4\text{H}_{10}\) into CO\(_2\). For example, the IFT between CO\(_2\) and heavy oil at 1101 kPa and 21.0°C is reduced from 28.31 mN/m to 16.07 mN/m by adding 18.5 mol% \(n\)-\(\text{C}_4\text{H}_{10}\) into the CO\(_2\) stream. The mechanistic parachor model is able to predict the equilibrium IFT for the CO\(_2\)-\(n\)-\(\text{C}_4\text{H}_{10}\)-heavy oil system with a good accuracy.

FIGURE 5-8 compares the measured and calculated equilibrium IFTs for the \(\text{C}_3\text{H}_8\)-\(n\)-\(\text{C}_4\text{H}_{10}\)-heavy oil system. The addition of \(n\)-\(\text{C}_4\text{H}_{10}\) into \(\text{C}_3\text{H}_8\) leads to a reduction of the equilibrium IFT for the \(\text{C}_3\text{H}_8\)-heavy oil system, though the reduction effect is not as significant as that for CO\(_2\)-heavy oil system. For example, the IFT of the \(\text{C}_3\text{H}_8\)-heavy oil system at 401 kPa and 21.0°C is reduced from 20.09 mN/m to 17.99 mN/m by adding
FIGURE 5-7: Comparison of the measured and calculated equilibrium IFT using Equation [5-11] for the CO$_2$-heavy oil system, CO$_2$-$n$-C$_4$H$_{10}$-heavy oil system (i.e., Mixture #4), and $n$-C$_4$H$_{10}$-heavy oil system at 21.0°C, respectively. The composition of Mixture #4 is (81.5 mol% CO$_2$, 18.5 mol% $n$-C$_4$H$_{10}$)
FIGURE 5-8: Comparison of the measured and calculated equilibrium IFT using Equation [5-11] for the \( \text{C}_3\text{H}_8 \)-heavy oil system, \( \text{C}_3\text{H}_8-\text{n-C}_4\text{H}_{10} \)-heavy oil system (i.e., Mixtures #5 and #6), and \( \text{n-C}_4\text{H}_{10} \)-heavy oil system at 21.0°C, respectively. The compositions of Mixtures #5 and #6 are (76.8 mol% \( \text{C}_3\text{H}_8 \), 23.2 mol% \( \text{n-C}_4\text{H}_{10} \)) and (61.4 mol% \( \text{C}_3\text{H}_8 \), 38.6 mol% \( \text{n-C}_4\text{H}_{10} \)), respectively.
23.2 mol% \( n-C_4H_{10} \) into the \( C_3H_8 \) stream. A greater reduction of IFT is achieved with a larger fraction of \( n-C_4H_{10} \). The mechanistic parachor model cannot accurately reproduce the measured equilibrium IFTs for the \( C_3H_8-n-C_4H_{10} \)-heavy oil system. This is probably because the mechanistic parachor model provides fairly underestimated equilibrium IFTs for the \( n-C_4H_{10} \)-heavy oil system.

FIGURE 5-9 shows the measured and calculated equilibrium IFTs between heavy oil and Mixture #7 (93.0 mol% \( CO_2 \), 5.9 mol% \( C_3H_8 \), 1.1 mol% \( n-C_4H_{10} \)). Compared to the pure \( CO_2 \) case, the solvent mixture leads to a reduced IFT due to the presence of the rich solvents of \( C_3H_8 \) and \( n-C_4H_{10} \). For example, the IFT of the \( CO_2 \)-heavy oil system at 3101 kPa and 21.0°C is reduced from 19.92 mN/m to 15.28 mN/m by adding 5.9 mol% \( C_3H_8 \) and 1.1 mol% \( n-C_4H_{10} \) into the \( CO_2 \) stream. It can be seen from FIGURE 5-9 that there exists a good agreement between the measured and calculated IFT for Mixture #7. It is worthwhile mentioning that another effect of adding rich solvents into \( CO_2 \) is reduction of the dewpoint pressure of the gas phase. \( n-C_4H_{10} \) shows a larger reduction effect compared to \( C_3H_8 \). In practice, it is more desirable to keep the injected solvents at gaseous state other than liquid state in a solvent processes for heavy oil recovery from the pressure maintenance point of view (Upreti et al., 2007; Pathak et al., 2011). Therefore, the type and amount of the added rich solvents must be carefully determined in a solvent recovery process according to the specific reservoir temperature and pressure in order to avoid the occurrence of liquid solvent phase.

It has been demonstrated previously that addition of \( C_3H_8 \) and/or \( n-C_4H_{10} \) into \( CO_2 \) results in an obvious reduction of equilibrium IFT between \( CO_2 \) and heavy oil. Such reduced IFT is favourable for achieving an improved recovery performance in an
FIGURE 5-9: Comparison of the measured and calculated equilibrium IFT using Equation [5-11] for the CO$_2$-heavy oil system and CO$_2$-$C_3$H$_8$-$n$-$C_4$H$_{10}$-heavy oil system (i.e., Mixture #7) at 21.0°C, respectively. The composition of Mixture #7 is (93.0 mol% CO$_2$, 5.9 mol% C$_3$H$_8$, 1.1 mol% $n$-$C_4$H$_{10}$)
immiscible CO₂ flooding process because the reduced IFT will result in an increased ratio of viscous to capillary forces, i.e., capillary number. A higher recovery factor of heavy oil can be expected since the recovery factor generally increases with the capillary number (Nobakht et al., 2007).

5.5 Summary

Experimental measurements of the equilibrium IFT for CO₂-, C₃H₈- and n-C₄H₁₀-heavy oil systems indicate that, at the same temperature and pressure, n-C₄H₁₀ leads to the lowest IFT while CO₂ results in the highest IFT. Addition of rich solvent(s) C₃H₈ and/or n-C₄H₁₀ into CO₂ stream leads to an obvious reduction of IFT between CO₂ and the Lloydminster heavy oil, though the degree of IFT reduction is dependent on the amount of the rich solvent(s) added. The IFT reduction of CO₂-heavy oil system due to addition of rich solvent(s) results in an increased capillary number, which is beneficial for achieving a higher heavy oil recovery.

The PR EOS together with the new alpha function is incorporated into a mechanistic parachor model to determine the equilibrium IFT of solvent(s)-CO₂-heavy oils systems. It is found that the mechanistic parachor model with the optimized parachor of Lloydminster heavy oil and mass transfer exponent can be used to qualitatively reproduce the measured IFTs between solvent(s) and heavy oil in the liquid-vapour phase region.
CHAPTER 6 DETERMINATION OF THREE-PHASE BOUNDARIES OF SOLVENT(S)-CO\(_2\)-HEAVY OIL SYSTEMS UNDER RESERVOIR CONDITIONS

6.1 Introduction

Previous studies indicate that, in addition to the normally observed L\(_1\)V phase equilibria and L\(_1\)L\(_2\) phase equilibria, L\(_1\)L\(_2\)V phase equilibria may also occur in the solvent(s)-CO\(_2\)-heavy oil systems under reservoir conditions (Shaw and Zou, 2007; Talbi and Maini, 2008; Badamchi-Zadeh et al., 2009b). In a typical L\(_1\)L\(_2\)V phase equilibrium for solvent(s)-CO\(_2\)-heavy oil systems, the L\(_1\) phase refers to the high-density liquid phase which contains significant amount of both solvents and heavy oil. The L\(_2\) phase refers to the low-density liquid phase which is mainly composed of liquid solvents, while the V phase refers to the vapour phase which is mainly composed of gaseous solvents. Numerous efforts have been made available to study the three-phase behaviour in CO\(_2\)-light oil systems, in which high displacement efficiency can be achieved due to the presence of L\(_1\)L\(_2\)V phase behaviour (Orr et al., 1981; Orr et al., 1983; Okuno et al., 2011). However, few efforts have been made available to determine the L\(_1\)L\(_2\)V three-phase boundary of solvent(s)-CO\(_2\)-heavy oil systems under reservoir conditions (Badamchi-Zadeh et al., 2009b).

In this chapter, the L\(_1\)L\(_2\)V phase boundaries of one CO\(_2\)-heavy oil mixture, one \(n\)-C\(_4\)H\(_{10}\)-CO\(_2\)-heavy oil mixture and one C\(_3\)H\(_8\)-CO\(_2\)-heavy oil mixture in the pressure-temperature (\(P\)-\(T\)) diagram are determined by using a pressure-volume-temperature (PVT) setup. The PR EOS model with a modified alpha function and three previously developed
BIP correlations is employed to predict the $\text{L}_1\text{L}_2\text{V}$ phase boundaries for the aforementioned systems. Subsequently, the measured and predicted $\text{L}_1\text{L}_2\text{V}$ phase boundaries have been presented, analyzed, and discussed.

6.2 Experimental

6.2.1. Materials

The heavy oil sample, collected from the Lloydminster area in Saskatchewan, Canada, has molecular weight of 482 g/mol and specific gravity of 0.9997 g/cm$^3$. The compositional analysis result of the Lloydminster heavy oil is provided in TABLE 4-1. The viscosity equation of the heavy oil sample is given by Equation [4-1], while its density equation is given by Equations [4-4] and [4-5]. The gas solvents, CO$_2$, C$_3$H$_8$ and $n$-C$_4$H$_{10}$ (Praxair, Canada), used in the measurements have purities of 99.998 mol%, 99.99 wt%, and 99.5 wt%, respectively. The densities of saturated gas solvents can be calculated with Equation [4-6].

6.2.2. Experimental setup

As shown in FIGURE 4-2, all the PVT measurements for the solvent(s)-CO$_2$-heavy oil systems are performed by using a mercury-free DBR PVT system (PVT-0150-100-200-316-155, DBR, Canada). The detailed description regarding the DBR PVT system can be found in CHAPTER 4.

6.2.3. Experimental procedures

In this study, one CO$_2$-heavy oil mixture (Feed #13), one C$_3$H$_8$-CO$_2$-heavy oil mixture (Feed #14), and one $n$-C$_4$H$_{10}$-CO$_2$-heavy oil mixture (Feed #15) have been
prepared and tested, respectively. TABLE 6-1 lists the detailed compositions of these three mixtures. Prior to each test, the PVT cell and the inlet tubing are thoroughly cleaned with kerosene, flushed with the gas solvent that will be injected and finally evacuated by using a vacuum pump. Sufficient liquefied CO$_2$ and C$_3$H$_8$ are first stored in the transfer cylinders that are connected to the inlet tubing of the PVT cell. Then the air bath temperature is set to the pre-specified point for at least 12 h to ensure that the transfer cylinders and the PVT cell reach the same temperature. The $n$-C$_4$H$_{10}$ cylinder, which allows for direct withdrawal of liquid $n$-C$_4$H$_{10}$ from the cylinder, is also connected to the inlet tubing of the PVT cell.

As for the measurements of CO$_2$-heavy oil system (i.e., Feed #13), a large amount of liquid CO$_2$ is injected into the PVT cell just above its vapour pressure using a high-pressure syringe pump (500HP, Teledyne ISCO Inc., USA). The mass of the liquid CO$_2$ injected can be determined according to its density and its volume measured by the accurate cathetometer. The magnetic stirrer is turned on just after CO$_2$ injection. Then heavy oil is added to the PVT cell to constitute the composition of Feed #13. The volume of heavy oil injected can be determined to be the total volume minus the liquid solvent volume. No volume change can be assumed since the volume measurement is conducted right after the heavy oil is injected into the PVT cell. Then the mass of heavy oil added can also be determined. The magnetic stirrer is found to be able to work properly because of the presence of excessive CO$_2$ in the CO$_2$-heavy oil mixture. The CO$_2$-heavy oil mixture is vigorously stirred for 6 h prior to any further measurement.

The experimental procedure for measuring the L$_1$L$_2$V phase boundary for Feed #13 is briefly described as follows. Starting from a high pressure at which L$_1$L$_2$ phase
TABLE 6-1: Compositions of solvent(s)-CO$_2$-heavy oil systems examined in this study

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>Composition, wt%</th>
<th></th>
<th></th>
<th>Composition, mol%</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C$_3$H$_8$</td>
<td>$n$-C$<em>4$H$</em>{10}$</td>
<td>CO$_2$</td>
<td>Heavy oil</td>
<td>C$_3$H$_8$</td>
<td>$n$-C$<em>4$H$</em>{10}$</td>
</tr>
<tr>
<td>13</td>
<td>0.0</td>
<td>0.0</td>
<td>60.4</td>
<td>39.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>12.3</td>
<td>0.0</td>
<td>35.1</td>
<td>52.6</td>
<td>23.6</td>
<td>0.0</td>
</tr>
<tr>
<td>15</td>
<td>0.0</td>
<td>10.1</td>
<td>54.2</td>
<td>35.7</td>
<td>0.0</td>
<td>11.8</td>
</tr>
</tbody>
</table>
equilibrium exists, the system pressure is reduced in a discrete manner by using a high-pressure automatic positive-displacement pump (PMP-0500-1-10-MB-316-M4-C0, DBR, Canada). For each pressure step, the magnetic stirrer is kept on to rigorously stir the CO2-heavy oil mixture. It is experimentally found that 12 h is sufficient for the cell pressure to reach a stabilized value for each step. A moment after the stirrer is turned off, the equilibrium state of the mixture (e.g., L1L2 equilibrium, L1L2V equilibrium or L1V equilibrium) can be determined based on visual observations made upon the mixture.

Once all the measurements for Feed #13 have been completed, a certain amount of liquid $n$-C4H10 is added into Feed #13 to constitute the composition of the $n$-C4H10-CO2-heavy oil system (i.e., Feed #15). As for Feed #14, liquid C3H8 is first discharged into the PVT cell, followed by adding liquid CO2 into the PVT cell. Afterwards, a certain amount of heavy oil is added into the PVT cell to achieve the composition of Feed #14. Similarly, the same procedure, used for determining the L1L2V phase boundary for Feed #13 at the L1L2V-L1L2 boundary, is also applied for Feed #14 and #15, respectively. In this study, the pressure measurement, volume measurement, temperature measurement, and determination of mixture composition have uncertainties of ±3.5 kPa, ±1.59×10^{-2} cm³, ±0.1 K, and ±3.0 wt%, respectively.

6.3 Mathematical Formulation

6.3.1. PR EOS model

The PR EOS together with the new alpha function is used to describe the phase behaviour of solvent(s)-CO2-heavy oil systems. The detailed expressions of the PR EOS together with the modified alpha function Equation [3-21] can be found in CHAPTER 3.
In this study, the heavy oil sample is treated as a single pseudocomponent, while the specific gravity and molar mass are used as the two characterization parameters. The characterization method for the heavy oil sample is provided in CHAPTER 4. The critical properties of CO$_2$, C$_3$H$_8$, \(n\)-C$_4$H$_{10}$ and heavy oil can be found in TABLE 4-9. The BIP for a four-component fluid system which is comprised of CO$_2$, C$_3$H$_8$, \(n\)-C$_4$H$_{10}$ and heavy oil is shown in TABLE 4-6. The BIP Equations [4-18], [4-19] and [4-20] are used to calculate the BIPs for CO$_2$-heavy oil binary, C$_3$H$_8$-heavy oil binary, and \(n\)-C$_4$H$_{10}$-heavy oil binary, respectively at a given temperature.

**6.3.2. Determination of the L$_1$L$_2$V phase boundaries**

In general, the L$_1$L$_2$V phase boundaries for a multi-component system can be determined by using stability analysis in conjunction with two phase flash calculations. The multi-component system with a given feed will be split into two phases if the minimum tangent plane distance function (TPDF) is calculated to be negative (Baker et al., 1982). It has been shown that the traditional gradient-based method may fail in some cases due to the existence of multiple stationary points for the TPDF (Saber and Shaw, 2008).

In this chapter, the robust global optimization algorithm Dividing RECTangles approach (DIRECT) is used to perform the stability analysis (Saber and Shaw, 2008). Once stability results show that the feed is unstable, two-phase flash calculations will be executed. Stability analysis is again performed for the two phases resulted from the two phase flash calculations. It should be noted that it is only necessary to perform one run of stability analysis for any one of the two equilibrium phases (Li and Firoozabadi, 2010).
Similarly, the three-phase flash calculations are initiated once the stability analysis shows that the multi-component system is unstable in the two-phase state.

At a constant temperature for a given feed, the \( L_1L_2V-L_2V \) phase boundary and \( L_1L_2V-L_1L_2 \) boundary in \( P-T \) phase diagram can be determined by performing stability analysis and two phase flash calculation with the pressure varying along the isothermal line. Subsequently, the temperature is changed to another point at which the BIPs are recalculated, while stability analysis, two-phase flash calculation and possible three-phase flash calculation are repeated.

### 6.4 Results and Discussion

The measured three-phase boundary pressures for Feeds #13-15 are tabulated in TABLE 6-2. FIGURE 6-1 shows digital images of the typical phase equilibria captured for the \( C_3H_8-CO_2 \)-heavy oil system (Feed #14) at 298.55 K. As can be clearly seen from FIGURE 6-1, at the constant temperature of 298.55 K, the ternary \( C_3H_8-CO_2 \)-heavy oil mixture has experienced \( L_1V \) phase equilibrium, \( L_1L_2V \) phase equilibrium, and \( L_1L_2 \) phase equilibrium in a sequential order with an gradual increase in system pressure. As for a typical \( L_1L_2V \) phase equilibrium shown in FIGURE 6-1b, the \( L_1 \) phase refers to the high-density liquid phase which contains significant amount of both solvents (i.e., \( C_3H_8 \) and \( CO_2 \)) and heavy oil. The \( L_2 \) phase, i.e., the low-density liquid phase, mainly contains liquid solvents (i.e., \( C_3H_8 \) and \( CO_2 \)), while the \( V \) phase is mainly composed of gaseous solvents (i.e., \( C_3H_8 \) and \( CO_2 \)).
### TABLE 6-2: Raw experimental data obtained in this study

<table>
<thead>
<tr>
<th>Systems</th>
<th>Temperature, K</th>
<th>$L_1L_2V-L_1L_2$ boundary pressure, kPa</th>
<th>$L_1L_2V-L_1V$ boundary pressure, kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed #13</td>
<td>288.65</td>
<td>5175</td>
<td>5097</td>
</tr>
<tr>
<td></td>
<td>298.65</td>
<td>6508</td>
<td>6487</td>
</tr>
<tr>
<td></td>
<td>304.95</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
<tr>
<td>Feed #14</td>
<td>288.95</td>
<td>4640</td>
<td>4305</td>
</tr>
<tr>
<td></td>
<td>298.55</td>
<td>5610</td>
<td>5328</td>
</tr>
<tr>
<td></td>
<td>309.55</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
<tr>
<td>Feed #15</td>
<td>288.65</td>
<td>4595</td>
<td>3754</td>
</tr>
<tr>
<td></td>
<td>298.65</td>
<td>5560</td>
<td>4750</td>
</tr>
<tr>
<td></td>
<td>308.55</td>
<td>6718</td>
<td>5941</td>
</tr>
</tbody>
</table>
FIGURE 6-1: Digital images of typical phase equilibria captured for the C_3H_8-CO_2-heavy oil system (Feed #14): (a) L_1L_2 phase equilibrium at 298.55 K and 6501.0 kPa; (b) L_1L_2V phase equilibrium at 298.55 K and 5538.0 kPa; and (c) L_1V phase equilibrium at 298.55 K and 5306.0 kPa
6.4.1. CO\textsubscript{2}-heavy oil system

FIGURE 6-2 shows the measured L\textsubscript{1}L\textsubscript{2}V phase boundary together with the calculated one by using PR EOS with Equations [4-7] and [4-18] for CO\textsubscript{2}-heavy oil binary: Feed #13. FIGURE 6-2 also includes the measured $K$ points (where the L\textsubscript{2} phase and V phase becomes identical) for four CO\textsubscript{2}-heavy alkane binaries, i.e., CO\textsubscript{2}-n-C\textsubscript{14}H\textsubscript{30} binary, CO\textsubscript{2}-C\textsubscript{15}H\textsubscript{32} binary, CO\textsubscript{2}-n-C\textsubscript{19}H\textsubscript{40} binary and CO\textsubscript{2}-n-C\textsubscript{21}H\textsubscript{44} binary (Miller and Luks, 1989). Similar to the CO\textsubscript{2}-heavy alkane binaries, emergence of three-phase coexistence in a CO\textsubscript{2}-heavy oil binary is attributed to the presence of excessive CO\textsubscript{2} concentration in the binary mixture. It can be seen from FIGURE 6-2 that the L\textsubscript{1}L\textsubscript{2}V phase boundary of CO\textsubscript{2}-heavy oil binary spans within a narrow region on the P-T phase diagram which is close to the vapour pressure line of pure CO\textsubscript{2}. For example, there is only a pressure difference of 78.0 kPa between the L\textsubscript{1}L\textsubscript{2}V-L\textsubscript{1}L\textsubscript{2} phase boundary and the L\textsubscript{1}L\textsubscript{2}V-L\textsubscript{1}V phase boundary at 288.65 K. This small span is consistent with the findings in the literature (Kodal and Sayegh, 1992). Also, the L\textsubscript{1}L\textsubscript{2}V phase boundary becomes narrower with an increase in temperature.

It can also be found from FIGURE 6-2 that the L\textsubscript{1}L\textsubscript{2}V phase boundary is predicted to be a line, instead of a narrow area measured by the experiments (Sayegh \textit{et al.}, 1990; Kodal and Sayegh, 1992) by using the PR EOS with Equations [4-7] and [4-18]. This is because the heavy oil is characterized with only a single pseudocomponent in this study. The predicted L\textsubscript{1}L\textsubscript{2}V phase boundary, however, is close to the experimentally measured boundaries. The predicted ending point of the L\textsubscript{1}L\textsubscript{2}V phase boundary, i.e., the $K$ point, is also shown in FIGURE 6-2. The predicted $K$ point for the CO\textsubscript{2}-heavy oil binary is found to exist at a lower temperature than those measured $K$ points for the CO\textsubscript{2}-heavy alkane
FIGURE 6-2: Comparison of the measured $L_1L_2V$ phase boundary and the predicted $L_1L_2V$ phase boundary by using the PR EOS with Equations [4-7] and [4-18] for the general CO$_2$-heavy oil system: Feed #13
binaries. This is reasonable because the molecular weight of the heavy oil sample used in this study is larger than that of \( n-C_{21}H_{44} \), while the measured \( K \) point occurs at a lower temperature for a binary mixture containing \( \text{CO}_2 \) and a heavier alkane (Miller and Luks, 1989).

**6.4.2. \( C_3H_8-\text{CO}_2 \)-heavy oil system**

FIGURE 6-3 compares the measured \( L_1L_2V \) phase boundary and the predicted \( L_1L_2V \) phase boundary with Equations [4-7], [4-18] and [4-19] for the ternary \( C_3H_8-\text{CO}_2 \)-heavy oil system: Feed #14. It can be apparently observed from FIGURE 6-3 that, at the same temperature, the measured \( L_1L_2V \) phase equilibria of the ternary \( C_3H_8-\text{CO}_2 \)-heavy oil system occur at a lower pressure compared to those of the \( \text{CO}_2 \)-heavy oil system. The pressure range of the measured \( L_1L_2V \) phase boundary of the ternary \( C_3H_8-\text{CO}_2 \)-heavy oil system spans within a wider area compared to that of the binary \( \text{CO}_2 \)-heavy oil system.

In general, the \( L_1L_2V \) phase boundary of the \( C_3H_8-\text{CO}_2 \)-heavy oil system is inclined to move to the higher-temperature and lower-pressure side of the \( P-T \) diagram if the \( L_1L_2V \) phase boundary of \( \text{CO}_2 \)-heavy oil system is considered as the reference for comparison. Such an observation is consistent with the three-phase boundary measurements made on a \( C_3H_8-\text{CO}_2 \)-Athabasca bitumen system in the literature (Badamchi-Zadeh et al., 2009b).

It can be also found from FIGURE 6-3 that the measured \( L_1L_2V-L_1L_2 \) phase boundary for the ternary \( C_3H_8-\text{CO}_2 \)-heavy oil system agrees well with the predicted \( L_1L_2V-L_1L_2 \) phase boundary, though the predicted \( L_1L_2V-L_1V \) phase boundary is slightly lower than its measured boundary. The predicted three-phase envelope for the ternary \( C_3H_8-\text{CO}_2 \)-heavy oil system also shrinks with an increase in temperature and terminates
FIGURE 6-3: Comparison of the measured L$_1$L$_2$V phase boundary and the predicted L$_1$L$_2$V phase boundary with Equations [4-7], [4-18] and [4-19] for the ternary C$_3$H$_8$-CO$_2$-heavy oil system: Feed #14
at the $K$ point, where the $L_2$ phase and $V$ phase become identical and coexist with the $L_1$ phase. The effect of adding $C_3H_8$ to $CO_2$ stream on the $L_1L_2V$ phase equilibria is in good agreement with the observed effect of adding $C_3H_8$ to $CO_2$ stream on the three-phase $L_1L_2V$ immiscibility of $CO_2-n-C_{19}H_{40}$ feed (Fall and Luks, 1986). The measured $L_1L_2V$ equilibria of $C_3H_8-CO_2-n-C_{19}H_{40}$ mixture also tend to move to the high-temperature and lower-pressure side of the $P-T$ diagram and cover a larger area compared to the $L_1L_2V$ equilibria of $CO_2-n-C_{19}H_{40}$ mixture. This effect is mainly attributed to the fact that $C_3H_8$ is highly soluble in both $CO_2$ and $n-C_{19}H_{40}$, leading to the partition of $L_1L_2V$ three phases at the extended temperature and pressure ranges (Saber and Shaw, 2009).

6.4.3. $n-C_4H_{10}-CO_2$-heavy oil system

FIGURE 6-4 compares the measured $L_1L_2V$ phase boundary and the predicted $L_1L_2V$ phase boundary by using the PR EOS with Equations [4-7] [4-18] and [4-20] for the ternary $n-C_4H_{10}-CO_2$-heavy oil system: Feed #15. Again, the pressure range of the measured $L_1L_2V$ phase boundary of the ternary $n-C_4H_{10}-CO_2$-heavy oil system spans within a wider area compared to that of the binary $CO_2$-heavy oil system. The $L_1L_2V$ phase boundary of the $n-C_4H_{10}-CO_2$-heavy oil system is also located at the higher-temperature and lower-pressure side of the $P-T$ diagram compared to the $L_1L_2V$ phase boundary of $CO_2$-heavy oil system. FIGURE 6-4 demonstrates that there exists a generally good agreement between the measured $L_1L_2V$ phase boundary and the predicted $L_1L_2V$ phase boundary by using the PR EOS with the Equations [4-7], [4-18] and [4-20] for the ternary $n-C_4H_{10}-CO_2$-heavy oil system. It can be also seen from FIGURE 6-4 that the predicted three-phase envelope shrinks with an increase in
FIGURE 6-4: Comparison of the measured L₁L₂V phase boundary and the predicted L₁L₂V phase boundary by using the PR EOS with Equations [4-7], [4-18] and [4-20] for the ternary $n$-C₄H₁₀-CO₂-heavy oil system: Feed #15
temperature and finally disappears at the $K$ point, where the L$_2$ phase and V phase become identical and coexist with the L$_1$ phase.

FIGURE 6-5 shows the calculated phase volumes and phase compositions for 1 mole feed with the composition of Feed #15 as a function of pressure at 298.65 K. The phase stability, two-phase flash and three-phase flash calculations are performed by using the volume-translated PR EOS with Equations [4-7], [4-18] and [4-20] for the ternary $n$-C$_4$H$_{10}$-CO$_2$-heavy oil system. As can be clearly seen from FIGURE 6-5a, the L$_2$ phase emerges at the L$_1$L$_2$V-L$_1$V boundary pressure, while the V phase disappears at the L$_1$L$_2$V-L$_1$L$_2$ boundary pressure. This is consistent with the visual observations during the measurements. In addition, the phase compositions shown in FIGUREs 6b, c, and d, indicate that, if three phases are coexisting, only trace of heavy oil is present in the V phase and L$_2$ phase, while a significant amount of CO$_2$ and $n$-C$_4$H$_{10}$ is dissolved in heavy oil in the L$_1$ phase.

Overall, it can be concluded from above discussion that addition of an alkane solvent, either C$_3$H$_8$ or $n$-C$_4$H$_{10}$, can lead to the existence of three-phase L$_1$L$_2$V equilibria over an extended temperature and pressure ranges. These temperature and pressure conditions are close to the *in-situ* conditions of typical heavy oil reservoirs. This implies that, when a solvent mixture composed of an alkane solvent and CO$_2$ is injected into heavy oil formations, three-phase L$_1$L$_2$V phase equilibria are highly likely to occur under reservoir conditions (Talbi and Maini, 2008). Such occurred three-phase equilibria should be taken into account when injection of solvent(s)-CO$_2$ mixture is considered for recovering heavy oil in hydrocarbon reservoirs.
FIGURE 6-5: (a) Calculated phase volumes for 1 mole of Feed #15 as a function of pressure at 298.65 K; Correspondingly calculated phase compositions as a function of pressure at 298.65 K; (b) V phase; (c) L₂ phase; and (d) L₁ phase. The phase behaviour calculations are performed by using the volume-translated PR EOS (Peneloux et al., 1982) with Equations [4-7], [4-18] and [4-20] for the ternary $n$-C₄H₁₀-CO₂-heavy oil system
Recent studies prove that adding alkane solvent C$_3$H$_8$ into CO$_2$ stream is able to significantly improve the recovery performance of CO$_2$ flooding in heavy oil formations (Talbi and Maini, 2008; Luo et al., 2012). Such an improvement is achieved based on several important mechanisms which mainly encompass the enhanced swelling effect and viscosity reduction of heavy oil, and IFT reduction between gas mixture and heavy oil. In addition to these established mechanisms, it is possible that the observed three-phase L$_1$L$_2$V equilibria of the solvent(s)-CO$_2$-heavy oil systems may also play an important role in improving the heavy oil recovery performance of solvent-enriched CO$_2$ flooding processes (Okuno et al., 2011; Feizabadi et al., 2012).

6.5 Summary

The L$_1$L$_2$V three-phase boundaries of one CO$_2$-heavy oil mixture, one $n$-C$_4$H$_{10}$-CO$_2$-heavy oil mixture and one C$_3$H$_8$-CO$_2$-heavy oil mixture are experimentally and theoretically determined under reservoir conditions. It is found that L$_1$L$_2$V phase equilibria occur in the CO$_2$-heavy oil system due mainly to the presence of excessive CO$_2$. It is found that adding an alkane solvent, either C$_3$H$_8$ or $n$-C$_4$H$_{10}$, to the CO$_2$-heavy oil system tends to expand the pressure span of the L$_1$L$_2$V phase boundary. Also, the measured L$_1$L$_2$V phase boundaries of the solvent(s)-CO$_2$-heavy oil system is found to be located at the higher-temperature and lower-pressure side of the $P$-$T$ diagram compared to the measured L$_1$L$_2$V phase boundary of CO$_2$-heavy oil system.

The extended span of L$_1$L$_2$V phase boundary observed for the solvent(s)-CO$_2$-heavy oil system indicates that three phase behaviour may occur over a wide range of temperature and pressure conditions when solvent(s)-CO$_2$ mixture is injected into heavy
oil reservoirs. The PR EOS with the modified alpha function and the BIP correlations, previously developed for CO$_2$-heavy oil binary, C$_3$H$_8$-heavy oil binary, and n-C$_4$H$_{10}$-heavy oil binary, respectively, is able to provide a generally good prediction of the measured L$_1$L$_2$V phase boundaries of the solvent(s)-CO$_2$-heavy oil systems under reservoir conditions.
CHAPTER 7 DETERMINATION OF MOLECULAR DIFFUSION COEFFICIENTS OF SOLVENT(S)-CO$_2$ MIXTURES IN HEAVY OIL

7.1 Introduction

Phase behaviour of solvent(s)-CO$_2$-heavy oil systems needs to be studied at equilibrium conditions. Intrusive forces can be applied in laboratory experiments to significantly accelerate the mass transfer between solvent(s)-CO$_2$ mixture and heavy oil. These intrusive forces are normally not available in the reservoir. The *in-situ* mass transfer between gas mixture and heavy oil under reservoir conditions are dominated by molecular diffusion and dispersion (Sayegh and Maini, 1984; Knorr and Imran, 2011). The magnitude of molecular diffusion coefficients affects the time for the heavy oil to achieve desirable viscosity reduction and swelling effect, thus influencing the oil production response (Boustani and Maini, 2001; Frauenfeld *et al.*, 2006). It is of fundamental and practical importance to determine the molecular diffusion coefficients of the solvent(s)-CO$_2$ mixture in heavy oil, allowing for accurate reservoir simulation and sound field development design.

In this study, a PVT experimental setup is used to conduct molecular diffusion tests to determine the individual molecular diffusion coefficient of each component in a gas mixture in heavy oil under reservoir conditions. During the diffusion tests, the gas mixture is allowed to naturally diffuse into heavy oil. Both the pressure- and volume-history of either gas or liquid phase are simultaneously recorded. Compositions of the gas
phase are measured before and after the diffusion test, respectively. Such determined molecular diffusion coefficients allow for more accurate determination of the rate and amount of solvent(s)-CO₂ mixture to be used in the huff cycle of a huff-\textit{n}-puff process.

7.2 Experimental

7.2.1. Materials

The Lloydminster heavy oil sample has molecular weight of 482 g/mol and specific gravity of 999.7 kg/m³. TABLE 4-1 shows the compositional analysis result of the Lloydminster heavy oil. The viscosity and density of the heavy oil sample are given by Equation [4-1] and [4-4], respectively. The viscosity of the Lloydminster heavy oil is 12854 cP at the test temperature of 294.55 K according to Equation [4-1]. The three gases, i.e., CO₂, C₃H₈ and \textit{n}-C₄H₁₀ (Praxair, Canada), have purities of 99.998 mol\%, 99.99 wt\%, and 99.5 wt\%, respectively.

7.2.2. Experimental setup

As shown in FIGURE 7-1, the molecular diffusion tests for the solvent(s)-CO₂-heavy oil systems are performed by using a DBR PVT system (PVT-0150-100-200-316-155, DBR, Canada). Detailed descriptions regarding the DBR PVT system can be found in CHAPTER 4.

7.2.3. Experimental procedures

Molecular diffusion tests have been performed for one pure CO₂-heavy oil system, one C₃H₈-CO₂-heavy oil system, and one \textit{n}-C₄H₁₀-CO₂-heavy oil system, respectively.
FIGURE 7-1: Schematic of PVT system for conducting molecular diffusion experiments
TABLE 7-1 shows the overall composition of these three systems together with the initial conditions of the molecular diffusion test. The first two tests are performed at similar pressures for comparison purpose.

The following section briefly describes the experimental procedure for the pure CO₂-heavy oil system. As shown in FIGURE 7-1, the isolation piston is first placed closer to the bottom of PVT cell, while the inlet valve of the PVT cell close to the hydraulic side is closed. Prior to each diffusion test, the PVT cell is tested for leakage with high-pressure nitrogen. The PVT cell and inlet tubing are then thoroughly cleaned with kerosene and flushed with air. A certain amount of heavy oil is gently introduced into the PVT cell. After the injection of heavy oil, it is necessary to increase the temperature to 338.15 K for 12 hours, allowing the heavy oil which is previously adhered to its wall for completely slipping downwards to the bulk heavy oil phase inside the PVT cell. Subsequently, the air-bath temperature is set to the test temperature of 294.55 K for at least 12 hours.

The PVT cell and tubing is vacuumed with the vacuum pump down to -60 kPa (gauge pressure) only to avoid possible upward movement of the piston. Once completed, the valve connected to the vacuum pump is closed and pure CO₂ is introduced directly from the transfer cylinder into the PVT cell. When the inlet valve is closed, pressure inside the PVT cell is recorded continuously using a high-precision pressure sensor (PM Series, 5000 psia, Heise, USA) with a full-scale accuracy of 0.025%. Meanwhile, the gas-phase volume and liquid-phase volume are measured simultaneously by tracking the upper gas-oil interface and the lower piston-hydraulic-oil interface. The test is terminated after 168 hours.

As for the experimental procedure for the C₃H₈-CO₂-heavy oil system, the C₃H₈-CO₂
**TABLE 7-1:** Overall compositions for the three feeds and initial conditions of the three diffusion tests

<table>
<thead>
<tr>
<th>Feed No.</th>
<th>System</th>
<th>Initial pressure, kPa</th>
<th>Temperature, K</th>
<th>Composition</th>
<th>Initial phase volume, cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>CO$_2$-heavy oil</td>
<td>3741</td>
<td>294.55</td>
<td>(74.05 mol% CO$_2$, 25.95 mol% heavy oil)</td>
<td>(79.1144 cm$^3$ CO$_2$, 27.2540 cm$^3$ heavy oil)</td>
</tr>
<tr>
<td>17</td>
<td>C$_3$H$_8$-CO$_2$-heavy oil</td>
<td>3799</td>
<td>294.55</td>
<td>(11.28 mol% C$_3$H$_8$, 60.94 mol% CO$_2$, 27.78 mol% heavy oil)</td>
<td>(54.3416 cm$^3$ C$_3$H$_8$+CO$_2$, 22.6324 cm$^3$ heavy oil)</td>
</tr>
<tr>
<td>18</td>
<td>n-C$<em>4$H$</em>{10}$-CO$_2$-heavy oil</td>
<td>1128</td>
<td>294.55</td>
<td>(4.71 mol% n-C$<em>4$H$</em>{10}$, 35.67 mol% CO$_2$, 59.62 mol% heavy oil)</td>
<td>(77.8826 cm$^3$ n-C$<em>4$H$</em>{10}$+CO$_2$, 27.9041 cm$^3$ heavy oil)</td>
</tr>
</tbody>
</table>
transfer cylinder is placed vertically prior to the mixing. Firstly, C\textsubscript{3}H\textsubscript{8} fills the vacuumed transfer cylinder by pushing the floating piston downward, resulting in a certain pressure. Next, CO\textsubscript{2} is released into the cylinder to mix with C\textsubscript{3}H\textsubscript{8} that is already contained in the cylinder, resulting in a higher pressure. With a sufficient duration of static mixing for 12 hours, the top valve of the transfer cylinder is opened. The C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2} mixture then flows into the vacuumed PVT cell and a 10 cm\textsuperscript{3} sampler (Swagelok, Canada, 1000 psi) simultaneously. When the inlet valve of the PVT cell is closed, the sampler is detached for gas-composition analysis with a high-precision gas chromatography (GC) analyzer (Model No.: 6890N, Agilent). Once the diffusion test is finished, the gas mixture in the PVT cell is sampled again for the compositional analysis. The sampling of the gas mixture from the beginning to the end of the test is able to quantitatively reflect the change in gas-phase composition during the diffusion test. The same experimental procedure is followed for the \textit{n}-C\textsubscript{4}H\textsubscript{10}-CO\textsubscript{2}-heavy oil system.

7.3 Mathematical Formulation

7.3.1. Mass transfer model

FIGURE 7-2 shows a schematic of molecular diffusion of a gas into heavy oil in a closed cell. The following assumptions are considered for the mass transfer model in this study: 1) The whole diffusion test can be considered an isothermal process since the environment temperature is controlled within the accuracy of ±0.1 K; 2) one-dimensional and one-way diffusion from gas phase to heavy oil (Jamialahmadi \textit{et al.}, 2006; Tharanivasan \textit{et al.}, 2006); and 3) the quasi-equilibrium boundary condition exists at the gas-liquid interface at a given pressure and temperature (Tharanivasan \textit{et al.}, 2006).
FIGURE 7-2: Schematic of dynamic process of molecular diffusion of the solvent(s)-CO₂ mixture into heavy oil in a closed PVT cell at a constant temperature
Based on the Fick’s second law, the mass transfer from the \( i \)th solvent component in a mixture to heavy oil is described by,

\[
\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}
\]  

[7-1]

where \( c_i \) is concentration of the \( i \)th solvent component in heavy oil in mole fraction, \( D_i \) is the individual molecular diffusion coefficient of the \( i \)th component in heavy oil, \( t \) is time, and \( x \) is distance from the bottom of the diffusion cell as shown in FIGURE 7-2. The molecular diffusion coefficients are assumed to be constant, considering that the duration of each molecular diffusion test is relatively short (i.e., 168 hours) and the solvent(s)-CO\(_2\) concentration in heavy oil is relatively low. Assuming constant molecular diffusion coefficients also facilitates easier comparison with the published data.

Since no solvent is dissolved in heavy oil at the beginning, the initial condition is,

\[
c_i = 0, \ 0 \leq x \leq L_0, \ t = 0
\]  

[7-2a]

where \( L_0 \) is initial height of heavy oil. The Neumann boundary condition can be applied at the impermeable bottom,

\[
\frac{\partial c_i}{\partial x} = 0, \ x = 0, \ t > 0
\]  

[7-2b]

The Dirichlet quasi-equilibrium boundary condition at the gas-liquid interface is given by,

\[
c_i = c_{i, \text{sat}} \left[ P(t) \right], \ x = L(t), \ t > 0
\]  

[7-2c]

where \( c_{i, \text{sat}} \) is saturation concentration of the \( i \)th gas component in heavy oil at current pressure \( P(t) \) and temperature, and \( L(t) \) is the height of the gas-diluted heavy oil at a given time. The saturation concentrations at the gas-liquid boundary can be determined...
by performing two-phase flash calculations for the overall feed at a given pressure and
temperature. It should be noted that this statement is only valid when the feed is found to
be unstable and phase split calculation is required (Baker et al., 1982). This is the case for
all the three diffusion tests in this study. The two-phase flash calculations are performed
with the volume-translated PR EOS. As for the Lloydminster heavy oil sample examined
in this study, the PR EOS and BIP correlations described by Equations [3-1]-[3-4] in
CHAPTER 3 and Equations [4-7]-[4-20] in CHAPTER 4 are able to provide reliable
estimates of the saturation concentration at the interface because these BIP correlations
have been validated with the measured phase behaviour data. The BIP matrix used is
shown in TABLE 4-6.

The mole fraction of each component $x_i$ in the liquid phase can be determined by
integrating the concentration along the diffusion direction,

$$ x_i = \frac{1}{L(t)} \int_0^{L(t)} c_i dx $$  \[7-3\]

Once the liquid-phase molar volume is obtained, its height can be updated for the
next iteration by,

$$ L(t) = V_{\text{corrected}} \sum_{j=1}^{nc} \frac{n_j}{A} $$ \[7-4\]

where $n_j$ is molar mass of the $j$th component in liquid phase, which is calculated via the
volume-translated PR EOS model. $A$ is cross-sectional area of the diffusion cell.

The swelling effect of heavy oil due to solvent dissolution can be quantified by
swelling factor. Similar to the definitions in the literature (Teja and Sandler, 1980), the
swelling factor in this study can be redefined as,
\[ SF(t) = \frac{V(t)}{V_0} \times \frac{1}{1 - X(t)} = \frac{V(t)}{V_0} \times \frac{1}{1 - \sum_{i=1}^{ag} x_i(t)} \]  \[ 7-5 \]

where \( V_0 \) is molar volume of heavy oil at the beginning of the pressure decay experiment, \( V(t) \) is molar volume of solvent-diluted heavy oil at a given pressure and temperature, and \( X(t) \) is mole fraction of gas solvent in heavy oil. \( V_1 \) and \( V(t) \) are updated with the volume-translated PR EOS.

### 7.3.2. Determination of molecular diffusion coefficients

Numerical calculation is performed to determine the individual molecular diffusion coefficient of each component of a gas mixture in heavy oil. FIGURE 7-3 shows a schematic for domain discretization, where \( c_{m,n} \) at the \( m \)th node and \( n \)th time step in the centre of the control domain (dashed area) is considered to be the characteristic mean value of this control domain.

The temporal term in Equation [7-1] is discretized with the first-order forward difference method,

\[ \frac{\partial c}{\partial t} \bigg|_{m,n} = \frac{c_{m+1} - c_{m}}{\Delta t} \]  \[ 7-6 \]

The diffusion term in Equation [7-1] is discretized with the second-order central difference method,

\[ \frac{\partial^2 c}{\partial x^2} \bigg|_{m,n} = \frac{c_{m+1} - 2c_{m} + c_{m-1}}{\Delta x^2} \]  \[ 7-7 \]

where \( m \) is the \( m \)th node along \( x \) direction, and \( n \) is the \( n \)th time step.

FIGURE 7-4 shows the procedure for determining the individual molecular diffusion
FIGURE 7-3: Schematic of domain discretization
FIGURE 7-4: Flowchart of determining the individual molecular diffusion coefficients
coefficients of each component in a gas mixture in heavy oil. The detailed procedure is described as follows:

1) Assume an initial molecular diffusion coefficient for each component in the gas mixture;

2) Based on the measured decaying pressure versus time, develop an accurate correlation between the decaying pressure and time, which will be used to determine the current pressure and then calculate the interface saturation concentration of each component at this pressure by performing two-phase flash calculation;

3) Solve the concentration of each component along $x$ direction with Equations [7-1]-[7-2c];

4) Use the volume-translated PR EOS model to update the molar volume of the solvent-diluted heavy oil by using Equations [3-1]-[3-4] and [4-7]-[4-14];

5) Update the liquid-phase height with Equation [7-4];

6) Calculate the swelling factor with Equation [7-5];

7) Repeat Steps #2-6 by using the updated data;

8) At the end of the diffusion test at $t=168$ h, the following objective function $O(c)$ is evaluated with the assumed diffusion coefficients. The objective function for both pure gas-heavy oil system and gas mixture-heavy oil system can be expressed by,

$$O(c) = \sqrt{\frac{1}{ng} \sum_{j=1}^{ng} (x_j^{\text{cal}} - x_j^{\text{exp}})^2}$$  \hspace{1cm} [7-8]
where $n_g$ is the number of gas-phase components, $x_i^{\text{cal}}$ and $x_i^{\text{exp}}$ are the calculated and measured mole fraction of the $i$th component in liquid phase at the end of the diffusion test, respectively;

9) If $O(c) \leq 10^{-5}$, terminate the calculation and consider the current diffusion coefficients as the optimum one for each component. If $O(c) > 10^{-5}$, another set of molecular diffusion coefficients should be assumed for next iteration by repeating Steps #2-8. The new molecular diffusion coefficients can be updated by the following successive substitution,

$$D_i^* = D_i \frac{x_i^{\text{exp}}}{x_i^{\text{cal}}}$$  \[7-9\]

10) After the individual molecular diffusion coefficients are obtained, repeat Steps #2-7 to calculate the swelling factor of heavy oil as a function of time.

The apparent molecular diffusion coefficient of a gas mixture can be obtained by assuming $D = D_1 = D_2$ for the two components in the gas mixture. In this study, the above procedure is then used to determine the apparent molecular diffusion coefficient unless Step #9 is changed to conduct one-dimensional exhaustive search of $D$ to achieve the minimum of Equation [7-8].

### 7.4 Results and Discussion

Before directly going to the measurement results, it is necessary to justify why an extremely long test is not required in this study to determine the molecular diffusion coefficients for a gas-mixture-heavy oil system. First of all, the soaking period during the
field application of solvent-based huff-n-puff processes is not extremely long, normally falling in the range of several hours to several days (Monger and Coma, 1988; Olenick et al., 1992). Thus, the molecular coefficients determined from an extremely long test might not be appropriate to be used for field huff-n-puff processes. In a traditional pressure-decay test, the system pressure experiences a long duration before reaching the so-called equilibrium pressure. However, there is no need to measure the decaying pressure data over an extremely long time if the experimental phase behaviour data, e.g., pressure versus solubility for a pure-gas-heavy oil system, are available (Tharanivasan et al., 2006). In addition, the measurement of the volume decay and gas-phase composition in this study, even during a short period, allows for more detailed understanding of the mass transfer mechanisms between gas phase and liquid phase.

In the case of a gas-mixture-heavy oil system, only two-phase flash calculation via an EOS model can provide the equilibrium saturation concentration in liquid phase at a given pressure because pressure-solubility relationship curve cannot be measured for a gas-mixture-heavy oil system. This is not the same as the case of a pure-gas-heavy oil system, in which, the solubility of pure gas in heavy oil can be measured as a function pressure. In this study, the PR EOS with the three BIP correlations has been validated with the measured phase behaviour data of solvent(s)-CO2-heavy-oil systems in CHAPTER 4. Therefore, the PR EOS model is able to provide reliable saturation-concentration calculations for the liquid phase that is required by the quasi-equilibrium boundary condition.
7.4.1. Diffusion profiles

*Pressure-decay profile:* FIGUREs 7-5, 7-6 and 7-7 display the measured pressure-decay history for the pure CO₂-heavy oil system, C₃H₈-CO₂-heavy oil system, and n-C₄H₁₀-CO₂-heavy oil system, respectively.

The pressure-decay history can be explicitly expressed as an exponential function of time with the following form (Zhang *et al.*, 2000; Tharanivasan *et al.*, 2006),

\[ P(t) = m_1 e^{-t/k_1} + m_2 e^{-t/k_2} + P_{eq} \]  \[ \text{[7-10]} \]

As for the pure CO₂-heavy oil system, C₃H₈-CO₂-heavy oil system, CO₂-n-C₄H₁₀-heavy oil system, the decaying pressure can be well described with the following fits with \( R^2=0.9997, R^2=0.9998 \) and \( R^2=0.9978 \), respectively,

\[
\begin{align*}
P(t)_{\text{CO}_2} &= 81.7014e^{-t/19551.7545} + 367.8442e^{-t/455580.8656} + 3276.3647 \\
P(t)_{\text{CO}_2-C_3H_8} &= 397.7363e^{-t/384911.4704} + 128.5204e^{-t/27765.4376} + 3268.1042 \\
P(t)_{\text{CO}_2-n-C_4H_{10}} &= 25.4486e^{-t/5000.6000} + 142.1509e^{-t/422083.4037} + 948.4474
\end{align*}
\]  \[ \text{[7-11a, b, c]} \]

where \( t \) is the diffusion time in s. The correlation coefficients of the three fits are all close to unity, indicating that Equation [7-10] is able to provide an excellent approximation for both the pure CO₂-heavy oil systems and for the solvent(s)-CO₂-heavy oil systems.

*Gas-phase volume-decay profile:* FIGURE 7-8 shows the measured gas-phase volume-decay profiles as a function of diffusion time for the three tests. It can be seen from FIGURE 7-8 that the gas-phase volume decreases slightly as diffusion proceeds for all the three tests, which is caused by the swelling of the heavy oil due to the gas dissolution. Apparently, the gas-phase volume-decaying history shown in FIGURE 7-8 appears to be much less obvious in comparison with the pressure-decaying profiles in FIGUREs 7-5 to 7-7.
FIGURE 7-5: Measured and correlated pressure-decay profile as a function of time for the CO$_2$-heavy oil system
FIGURE 7-6: Measured and correlated pressure-decay profile as a function of time for the C₃H₈-CO₂-heavy oil system.
FIGURE 7-7: Measured and correlated pressure decay profile as a function of time for the $n$-C$_4$H$_{10}$-CO$_2$-heavy oil system
FIGURE 7-8: Gas-phase volume-decay profiles as a function of time for the three diffusion tests
Gas-phase compositional changes: Although continuous monitoring of gas-phase composition has not been made possible in this study, the gas-phase compositions measured at the beginning and the end of the diffusion test are able to generally indicate the compositional change in the gas phase during the diffusion.

TABLE 7-2 shows the compositions of C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2} mixture and n-C\textsubscript{4}H\textsubscript{10}-CO\textsubscript{2} mixture measured at the beginning and the end of the diffusion test. The GC-analysis results indicate that no heavy hydrocarbon is detected in the gas phase after 168 hours of the diffusion test, confirming the one-dimensional and one-way diffusion assumed in this study. It can be also found from TABLE 7-2 that the concentration of gas solvent C\textsubscript{3}H\textsubscript{8} or n-C\textsubscript{4}H\textsubscript{10} shows a large decrease at the end of the diffusion test, compared to their initial values. Accordingly, CO\textsubscript{2} concentration increases at the end of the diffusion test. As for the C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2}-heavy oil system, C\textsubscript{3}H\textsubscript{8} concentration decreases from 15.62 mol\% to 9.96 mol\% after 168 hours of diffusion, while CO\textsubscript{2} concentration increases from 84.38 mol\% to 90.04 mol\%. Similarly, with regard to the n-C\textsubscript{4}H\textsubscript{10}-CO\textsubscript{2}-heavy oil system, the n-C\textsubscript{4}H\textsubscript{10} concentration decreases from 11.67 mol\% to 4.79 mol\% after 168 hours of diffusion, whereas the CO\textsubscript{2} concentration increases from 88.33 mol\% to 95.21 mol\%.

7.4.2. Molecular diffusion coefficients

Based on the multi-component diffusion model as described by Equation [7-1], the molecular diffusion coefficients for a pure gas or a gas mixture can be determined by minimizing the objective function Equation [7-8].

TABLE 7-3 shows the molecular coefficient of pure CO\textsubscript{2} in heavy oil at 294.55 K, the individual molecular diffusion coefficients of C\textsubscript{3}H\textsubscript{8} and CO\textsubscript{2} in heavy oil, and the individual molecular diffusion coefficients of n-C\textsubscript{4}H\textsubscript{10} and CO\textsubscript{2} in heavy oil, respectively.
**TABLE 7-2:** Compositional analysis results of C$_3$H$_8$-CO$_2$ mixture and \(n\)-C$_4$H$_{10}$-CO$_2$ mixture measured at the beginning and the end of the diffusion tests

<table>
<thead>
<tr>
<th>System</th>
<th>Beginning</th>
<th>End</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C$_3$H$_8$-CO$_2$ mixture</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>&lt;0.01 mol%</td>
<td>H$_2$</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;0.01 mol%</td>
<td>CO</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.08 mol%</td>
<td>N$_2$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>&lt;0.01 mol%</td>
<td>O$_2$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>84.25 mol%</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.06 mol%</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>&lt;0.01 mol%</td>
<td>C$_2$H$_4$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>&lt;0.01 mol%</td>
<td>C$_2$H$_6$</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>&lt;0.01 mol%</td>
<td>C$_3$H$_6$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>15.60 mol%</td>
<td>C$_3$H$_8$</td>
</tr>
<tr>
<td>(i)-C$<em>4$H$</em>{10}$</td>
<td>&lt;0.01 mol%</td>
<td>(i)-C$<em>4$H$</em>{10}$</td>
</tr>
<tr>
<td>(n)-C$<em>4$H$</em>{10}$</td>
<td>&lt;0.01 mol%</td>
<td>(n)-C$<em>4$H$</em>{10}$</td>
</tr>
<tr>
<td>C$_5$-</td>
<td>&lt;0.01 mol%</td>
<td>C$_5$-</td>
</tr>
<tr>
<td>C$_6$-</td>
<td>&lt;0.01 mol%</td>
<td>C$_6$-</td>
</tr>
<tr>
<td><strong>Rounded C$_3$H$_8$-CO$_2$ composition</strong></td>
<td>(15.62 mol% C$_3$H$_8$, 84.38 mol% CO$_2$)</td>
<td>(9.96 mol% C$_3$H$_8$, 90.04 mol% CO$_2$)</td>
</tr>
<tr>
<td><strong>n-C$<em>4$H$</em>{10}$-CO$_2$ mixture</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>&lt;0.01 mol%</td>
<td>H$_2$</td>
</tr>
<tr>
<td>CO</td>
<td>&lt;0.01 mol%</td>
<td>CO</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.23 mol%</td>
<td>N$_2$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>&lt;0.01 mol%</td>
<td>O$_2$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>88.10 mol%</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>&lt;0.01 mol%</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>&lt;0.01 mol%</td>
<td>C$_2$H$_4$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>&lt;0.01 mol%</td>
<td>C$_2$H$_6$</td>
</tr>
<tr>
<td>C$_3$H$_6$</td>
<td>0.02 mol%</td>
<td>C$_3$H$_6$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>0.01 mol%</td>
<td>C$_3$H$_8$</td>
</tr>
<tr>
<td>(i)-C$<em>4$H$</em>{10}$</td>
<td>&lt;0.01 mol%</td>
<td>(i)-C$<em>4$H$</em>{10}$</td>
</tr>
<tr>
<td>(n)-C$<em>4$H$</em>{10}$</td>
<td>11.64 mol%</td>
<td>(n)-C$<em>4$H$</em>{10}$</td>
</tr>
<tr>
<td>C$_5$-</td>
<td>&lt;0.01 mol%</td>
<td>C$_5$-</td>
</tr>
<tr>
<td>C$_6$-</td>
<td>&lt;0.01 mol%</td>
<td>C$_6$-</td>
</tr>
<tr>
<td><strong>Rounded (n)-C$<em>4$H$</em>{10}$-CO$_2$ composition</strong></td>
<td>(11.67 mol% (n)-C$<em>4$H$</em>{10}$, 88.33 mol% CO$_2$)</td>
<td>(4.79 mol% (n)-C$<em>4$H$</em>{10}$, 95.21 mol% CO$_2$)</td>
</tr>
</tbody>
</table>
**TABLE 7-3:** Comparison of the measured molecular diffusion coefficients in different oils

<table>
<thead>
<tr>
<th>Gas system</th>
<th>Heavy oil</th>
<th>Viscosity cP</th>
<th>Pressure kPa</th>
<th>Temperature K</th>
<th>Molecular diffusion Coefficient $10^{-10}$ m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ (this study)</td>
<td>Lloydminster heavy oil</td>
<td>12854 @ 294.55 K</td>
<td>3741-3371</td>
<td>294.55</td>
<td>8.24</td>
</tr>
<tr>
<td>CO₂ (Yang and Gu, 2006b)</td>
<td>Lloydminster heavy oil</td>
<td>23000 @ 297.05 K</td>
<td>2000-6000</td>
<td>297.05</td>
<td>2.00-5.50</td>
</tr>
<tr>
<td>CO₂ (Upreti and Mehrrota, 2000)</td>
<td>Athabasca bitumen</td>
<td>767 @ 353.15 K</td>
<td>3100-4100</td>
<td>298.15</td>
<td>1.60-2.20</td>
</tr>
<tr>
<td>CO₂ (Upreti and Mehrotra, 2002)</td>
<td>Athabasca bitumen</td>
<td>821000 @ 298.15 K</td>
<td>4000</td>
<td>298.15</td>
<td>1.20-2.00</td>
</tr>
<tr>
<td>CO₂ (Rasmussen and Civan, 2009)</td>
<td>Athabasca bitumen</td>
<td>106000 @ 313.15 K</td>
<td>4000-3240</td>
<td>348.15</td>
<td>5.03</td>
</tr>
<tr>
<td>CO₂ (Fadai et al., 2011)</td>
<td>Athabasca bitumen</td>
<td>~2000000 @ 294 K</td>
<td>3100-5600</td>
<td>294.15</td>
<td>1.20-2.40</td>
</tr>
<tr>
<td>C₃H₈ (Luo et al., 2007)</td>
<td>Lloydminster heavy oil</td>
<td>24137 @ 297.05</td>
<td>200-800</td>
<td>297.05</td>
<td>0.53-4.90</td>
</tr>
<tr>
<td>C₃H₈ (Yang and Gu, 2006b)</td>
<td>Lloydminster heavy oil</td>
<td>23000 @ 297.05 K</td>
<td>400-900</td>
<td>297.05</td>
<td>0.90-6.80</td>
</tr>
<tr>
<td>C₅H₈ (Ganapathi, 2009)</td>
<td>Lloydminster heavy oil</td>
<td>13144 @ 290 K</td>
<td>400-600</td>
<td>298</td>
<td>2.12-3.59</td>
</tr>
<tr>
<td>n-C₄H₁₀ (Ganapathi, 2009)</td>
<td>Lloydminster heavy oil</td>
<td>13144 @ 290 K</td>
<td>100-150</td>
<td>298</td>
<td>1.10-1.84</td>
</tr>
<tr>
<td>Gas mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(84.38 mol% CO₂, 15.62 mol% C₃H₈) (this study)</td>
<td>Lloydminster heavy oil</td>
<td>12854 cP @ 294.55 K</td>
<td>3799-3349</td>
<td>294.55</td>
<td>4.06 (CO₂) 13.34 (C₃H₈) 4.63*</td>
</tr>
<tr>
<td>(88.33 mol% CO₂, 11.7 mol% n-C₄H₁₀) (this study)</td>
<td>Lloydminster heavy oil</td>
<td>12854 cP @ 294.55 K</td>
<td>1128-982</td>
<td>294.55</td>
<td>1.92 (CO₂) 13.41 (n-C₄H₁₀) 2.88*</td>
</tr>
<tr>
<td>(70 mol% CO₂, 30 mol% C₃H₈) (Yang and Gu, 2006b)</td>
<td>Lloydminster heavy oil</td>
<td>23000 @ 297.05 K</td>
<td>1003-3005</td>
<td>297.05</td>
<td>0.82-8.20*</td>
</tr>
</tbody>
</table>

*Note: Apparent molecular diffusion coefficients of the gas mixture.
TABLE 7-3 also presents the molecular diffusion coefficients for pure CO₂, pure C₃H₈, pure n-C₄H₁₀ and one CO₂-C₃H₈ mixture in different heavy oils that are documented in the literature for comparison purpose. The molecular diffusion coefficient of pure CO₂ in heavy oil at the starting pressure of 3741 kPa and 294.55 K is measured to be 8.24×10⁻¹⁰ m²/s. This value is higher than the other literature values shown in TABLE 7-3 at similar conditions due probably to the lower viscosity of the Lloydminster heavy oil used in this study compared to the other oil samples in the literature.

As can be seen from TABLE 7-3, the individual molecular diffusion coefficients of CO₂ and C₃H₈ in heavy oil are determined to be 4.06×10⁻¹⁰ m²/s and 13.34×10⁻¹⁰ m²/s, respectively. Obviously, under the same pressure and temperature, C₃H₈ in the C₃H₈-CO₂ mixture diffuses faster into heavy oil than CO₂. Furthermore, it is interesting to note that the diffusivity of C₃H₈ (13.34×10⁻¹⁰ m²/s) measured at 294.55 K in this study is significantly larger than those measured in the literature at similar temperatures, e.g., 0.90×10⁻¹⁰-6.80×10⁻¹⁰ m²/s at pressure range of 400-900 kPa and 297.05 K (Yang and Gu, 2006b). The larger diffusivity of C₃H₈ measured in this study can be attributed to a higher pressure of the CO₂-C₃H₈ mixture used. It is well recognized in the literature that, at the same temperature, a higher pressure but lower than its dew point pressure leads to a higher diffusivity of C₃H₈ in heavy oil (Yang and Gu, 2006b; Luo et al., 2007). The starting pressure of 3799 kPa at 294.55 K in this study is greatly larger than the pressures at 297.05 K tested in the literature (Yang and Gu, 2006b; Luo et al., 2007), leading to a higher diffusivity of C₃H₈ in heavy oil. This implies one of the beneficial effects for using CO₂-C₃H₈ mixture instead of only C₃H₈. The presence of CO₂ in the CO₂-C₃H₈ mixture can make the dew point pressure of the CO₂-C₃H₈ significantly larger than that of pure
C₃H₈, allowing for a faster dissolution of solvent C₃H₈ into heavy oil. It can also be noted from TABLE 7-4 that, at the end of the diffusion test, a total of 35.92 mol% of C₃H₈-CO₂ mixture is dissolved in heavy oil, while a smaller fraction, 28.92 mol% of CO₂, is present in heavy oil. A larger fraction of gas components in heavy oil is able to provide larger swelling effect and viscosity reduction of heavy oil.

The individual molecular diffusion coefficients of CO₂ and n-C₄H₁₀ in heavy oil are determined to be 1.92×10⁻¹⁰ m²/s and 13.41×10⁻¹⁰ m²/s, respectively. Similarly, it is found that n-C₄H₁₀ in the n-C₄H₁₀-CO₂ mixture diffuses faster into heavy oil than CO₂. Compared to the literature data (Ganapathi, 2009), the larger diffusivity of n-C₄H₁₀ measured in this study can also be ascribed to a higher pressure of the CO₂-n-C₄H₁₀ mixture used in the diffusion test. However, one effect must be taken into account when adding n-C₄H₁₀ into CO₂ stream. Due to the low dew point pressure of n-C₄H₁₀, addition of n-C₄H₁₀ into CO₂ stream can significantly reduce the dew point pressure of n-C₄H₁₀-CO₂ mixture, and therefore induce the formation of liquid n-C₄H₁₀-CO₂ mixture under reservoir conditions.

As mentioned earlier, the apparent molecular diffusion coefficients can also be determined by minimizing the discrepancy between the measured and calculated mole fractions of solvent(s)-CO₂ mixture in heavy oil (See TABLE 7-3). TABLE 7-4 shows the measured and calculated mole fractions of solvent(s)-CO₂ mixture in heavy oil at the end of diffusion tests by both using the individual and apparent molecular diffusion coefficients. It can be seen from TABLE 7-4 that the individual molecular diffusion coefficients are able to provide far more accurate prediction of the mole fractions of solvent(s)-CO₂ in heavy oil at the end of diffusion tests. This is exactly the reason why
TABLE 7-4: Measured and calculated mole fractions of solvent(s)-CO$_2$ in heavy oil at the end of diffusion tests

<table>
<thead>
<tr>
<th>System</th>
<th>Measured*</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Using individual diffusion coefficients</td>
</tr>
<tr>
<td>Pure CO$_2$ in heavy oil</td>
<td>28.92 mol% CO$_2$</td>
<td>28.92 mol% CO$_2$</td>
</tr>
<tr>
<td>C$_3$H$_8$-CO$_2$ mixture in heavy oil</td>
<td>(13.01 mol% C$_3$H$_8$, 22.91 mol% CO$_2$)</td>
<td>(13.01 mol% C$_3$H$_8$, 22.92 mol% CO$_2$)</td>
</tr>
<tr>
<td>$n$-C$<em>4$H$</em>{10}$-CO$_2$ mixture in heavy oil</td>
<td>(4.55 mol% $n$-C$<em>4$H$</em>{10}$, 4.71 mol% CO$_2$)</td>
<td>(4.55 mol% $n$-C$<em>4$H$</em>{10}$, 4.71 mol% CO$_2$)</td>
</tr>
</tbody>
</table>

*Note: The mole fractions of solvent(s) and CO$_2$ in heavy oil are determined based on the composition change at the beginning and the end of the diffusion tests as shown in TABLE 7-2.
the molecular diffusion coefficient of each component in the mixture must be treated separately in the numerical model to generate a good match with the measured composition change during the diffusion test.

7.4.3. Swelling factor

Swelling effect is an important physical phenomenon when using a solvent(s)-CO2 mixture in heavy-oil recovery processes. FIGURE 7-9 shows the measured and calculated swelling factor as a function of diffusion time for the CO2-heavy oil system, C3H8-CO2-heavy oil system, and n-C4H10-CO2-heavy oil system, respectively. The calculated swelling factors are in generally good agreement with the measured ones. It can be seen from FIGURE 7-9 that, at the similar starting pressures, the C3H8-CO2-heavy oil system is able to provide a significantly larger swelling factor along the diffusion process in comparison with the CO2-heavy oil system.

The molecular diffusion of C3H8-CO2 mixture into heavy oil tends to accelerate the swelling of heavy oil, leading to a larger degree of swelling effect at the same diffusion time. The swelling factors of the C3H8-CO2-heavy oil system and the CO2-heavy oil system are measured to be 1.058 and 1.031 at the end of the diffusion test. Such enhanced swelling effect of the C3H8-CO2-heavy oil system is attributed to the fact that C3H8 diffuses faster into heavy oil than CO2 and that C3H8 is able to generate a larger swelling effect than CO2 when the same mole fractions of CO2 or C3H8 is dissolved in heavy oil (Yang and Gu, 2006b; Li et al., 2011). The swelling factor of the n-C4H10-CO2-heavy oil system is measured to be only 1.015 at the end of the diffusion test. This is ascribed to the fact that a low pressure of the n-C4H10-CO2 mixture used in the diffusion test can only lead to a small solubility of such a mixture in heavy oil even at equilibrium.
**FIGURE 7-9:** Measured and calculated swelling factor based on the individual molecular diffusion coefficients for the CO$_2$-heavy oil system, C$_3$H$_8$-CO$_2$-heavy oil system and n-C$_4$H$_{10}$-CO$_2$-heavy oil system
conditions. In addition to the mole fraction of a solvent in the solvent-CO₂ mixture, therefore, pressure is another important parameter to be considered in designing an efficient solvent(s)-CO₂-based huff-n-puff process. A higher operating pressure generally not only leads to a higher equilibrium solubility of the solvent(s)-CO₂ mixture in heavy oil (Li et al., 2011), but also enables a faster diffusion of the solvent(s)-CO₂ mixture into heavy oil. As such, more effective and efficient swelling effect and viscosity reduction can be achieved at a higher operating pressure.

7.5 Summary

Three diffusion experiments are conducted to determine the molecular diffusion coefficients for one CO₂-heavy oil system, one C₃H₈-CO₂-heavy oil system and one n-C₄H₁₀-CO₂-heavy oil system, respectively. GC-based composition analysis is performed to examine the composition change of gas phase during the diffusion test. During the diffusion tests, the gas-phase solvent fraction is found to decrease as diffusion proceeds, while the gas-phase CO₂ fraction decreases. As for the solvent-CO₂ mixtures tested, the molecular diffusion coefficient of solvent in heavy oil is found to be significantly larger than that of CO₂ in heavy oil.

The oil swelling is found to be significant when solvent-CO₂ mixture diffuses into heavy oil at a high pressure. At a similar starting pressure, the molecular diffusion of C₃H₈-CO₂ mixture into heavy oil tends to accelerate the swelling of heavy oil, leading to a larger degree of swelling effect after a given diffusion time, in comparison with pure CO₂. The individual molecular diffusion coefficients for C₃H₈-CO₂ in heavy oil are
determined to be $4.06 \times 10^{-10}$ m$^2$/s and $13.34 \times 10^{-10}$ m$^2$/s, respectively, at a starting pressure of 3799 kPa and 294.55 K. The individual molecular diffusion coefficients for $n$-C$_4$H$_{10}$-CO$_2$ in heavy oil are determined to be $1.92 \times 10^{-10}$ m$^2$/s and $13.41 \times 10^{-10}$ m$^2$/s, respectively, at a starting pressure of 1128 kPa and 294.55 K.
CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The major contributions of this dissertation can be summarized as follows.

1) A new alpha function in PR EOS is developed to more accurately predict the vapor pressure of non-hydrocarbons and hydrocarbon compounds. The acentric factor is redefined at a reduced temperature of 0.6 and incorporated into the newly developed alpha function. The new alpha function can be used to more accurately predict the vapour pressure for polar or nonpolar non-hydrocarbon substances, light hydrocarbons, and heavy hydrocarbons (up to \( n \)-tritetracontane) in comparison to the other existing alpha functions evaluated;

2) Well-designed experiments have been performed to measure saturation pressure, viscosity, interfacial tension, and multiphase boundaries of solvent(s)-CO\(_2\)-heavy oil systems at high pressures and elevated temperatures, while theoretical models have been developed to quantify them with a generally good accuracy; and

3) A theoretical and experimental framework is proposed to determine the individual molecular diffusion coefficient of each component of the solvent(s)-CO\(_2\) mixture in heavy oil under reservoir conditions. The preferential diffusion of either solvent(s) or CO\(_2\) in the solvent(s)-CO\(_2\) mixture can be accounted for with the proposed method because the composition change at the beginning and the end of the diffusion tests are measured.

Experimental and theoretical techniques have been developed to study the phase behaviour and mass transfer of solvent(s)-CO\(_2\)-heavy oil systems under reservoir
conditions. Experimentally, the saturation pressures, swelling factors, $L_1L_2V$ three-phase boundaries, and molecular diffusion coefficients of solvent(s)-CO$_2$-heavy oil systems have been measured by using a PVT setup, while the IFTs of solvent(s)-CO$_2$-heavy oil systems have been determined by using a ADSA technique. The following conclusions can be drawn based on the aforementioned experimental measurements,

1) It is experimentally found that significantly enhanced swelling effect and viscosity reduction of heavy oil can be obtained by adding either C$_3$H$_8$ or $n$-C$_4$H$_{10}$ into CO$_2$ stream. Adding either C$_3$H$_8$ or $n$-C$_4$H$_{10}$ into CO$_2$ can also cause the emergence of $L_1L_2V$ three phases under reservoir conditions. Under the same conditions, C$_3$H$_8$ and/or $n$-C$_4$H$_{10}$ is found to be much soluble in heavy oil compared to CO$_2$. A significantly increased swelling effect of heavy oil can be obtained by adding either C$_3$H$_8$ or $n$-C$_4$H$_{10}$ into CO$_2$ stream. An enhanced viscosity reduction of the CO$_2$-heavy oil system can also be achieved in the presence of either C$_3$H$_8$ or $n$-C$_4$H$_{10}$;

2) It is experimentally revealed that the addition of C$_3$H$_8$ and/or $n$-C$_4$H$_{10}$ into CO$_2$ stream can also lead to an obvious reduction of interfacial tension (IFT) between CO$_2$ and heavy oil. The measured equilibrium IFTs for CO$_2$-, C$_3$H$_8$- and $n$-C$_4$H$_{10}$-heavy oil systems indicate that, at the same temperature and pressure, $n$-C$_4$H$_{10}$ leads to the lowest IFT while CO$_2$ results in the highest IFT. Addition of rich solvent(s) C$_3$H$_8$ and/or $n$-C$_4$H$_{10}$ into CO$_2$ stream leads to an obvious reduction of IFT between CO$_2$ and heavy oil, though the degree of IFT reduction is dependent on the amount of the rich solvent(s) added. The IFT reduction of CO$_2$-heavy oil
system due to addition of rich solvent(s) results in an increased capillary number, which is beneficial for achieving a higher heavy oil recovery;

3) The L\textsubscript{1}L\textsubscript{2}V three-phase equilibria occur in the CO\textsubscript{2}-heavy oil system mainly because of the presence of excessive CO\textsubscript{2}. Adding an alkane solvent, either C\textsubscript{3}H\textsubscript{8} or n-C\textsubscript{4}H\textsubscript{10}, to the CO\textsubscript{2}-heavy oil system tends to expand the pressure span of the L\textsubscript{1}L\textsubscript{2}V phase boundary. The measured L\textsubscript{1}L\textsubscript{2}V phase boundaries of the solvent(s)-CO\textsubscript{2}-heavy oil system is found to be located at the higher-temperature and lower-pressure side of the $P$-$T$ diagram compared to the measured L\textsubscript{1}L\textsubscript{2}V phase boundary of CO\textsubscript{2}-heavy oil system. The extended span of L\textsubscript{1}L\textsubscript{2}V phase boundary observed for the solvent(s)-CO\textsubscript{2}-heavy oil system indicates that three-phase behaviour are highly likely to occur in-situ when solvent(s)-CO\textsubscript{2} mixture is injected into heavy oil reservoirs; and

4) The pressure-decay experiments for solvent(s)-CO\textsubscript{2}-heavy oil system indicate that the gas-phase solvent fraction decreases as diffusion proceeds, while the gas-phase CO\textsubscript{2} fraction increases during the test. As for the solvent(s)-CO\textsubscript{2} mixtures tested, the molecular diffusion coefficient of solvent in heavy oil is found to be significantly larger than that of CO\textsubscript{2} in heavy oil. In addition, at similar conditions, the C\textsubscript{3}H\textsubscript{8}-CO\textsubscript{2} mixture leads to an accelerated swelling-factor growth compared to pure CO\textsubscript{2}.

Theoretically, the PR EOS together with a new alpha function is employed as the fundamental model to describe the phase behaviour of solvent(s)-CO\textsubscript{2}-heavy oil systems.

The following conclusions can be drawn based on the aforementioned theoretical modelling efforts,
1) Three BIP correlations in PR EOS are proposed for characterizing CO$_2$-heavy oil binaries, C$_3$H$_8$-heavy oil binaries and $n$-C$_4$H$_{10}$-heavy oil binaries, respectively, by treating heavy oil sample as a single pseudocomponent with its molecular weight and specific gravity. The PR EOS together with the BIP correlations and the new alpha function is able to predict the saturation pressures and swelling factors and three-phase boundaries of the solvent(s)-CO$_2$-heavy oil systems with a generally good accuracy, though the prediction accuracy is slightly reduced at temperatures close to the critical temperature of a pure solvent;

2) The mechanistic parachor model with optimized parachor of Lloydminster heavy oil and mass transfer exponent can qualitatively represent the measured IFTs between solvent(s) and heavy oil in the liquid-vapour phase region; and

3) A one-dimensional and one-way diffusion model is developed to describe the molecular diffusion of solvent(s)-CO$_2$ mixture in heavy oil. The individual molecular diffusion coefficients for each component in the mixture can be determined by minimizing the discrepancy between the measured composition change and the calculated composition change with the diffusion model.

In summary, the important mechanisms, including significantly enhanced swelling effect and viscosity reduction of heavy oil, IFT reduction between solvent(s)-CO$_2$ mixture and heavy oil, and an accelerated growth in swelling factor, are shown to take place when solvent(s)-CO$_2$ mixture comes into contact with heavy oil. These beneficial mechanisms imply that many established CO$_2$-based heavy oil recovery methods, for example, CO$_2$ cyclic injection, CO$_2$ huff-$n$-puff, continuous CO$_2$ injection, and water-
alternating-CO₂ injection can be further improved or modified by adding an appropriate amount of gas alkanes into CO₂ stream.

### 8.2 Recommendations

The enhanced swelling effect and viscosity reduction caused by adding either C₃H₈ or n-C₄H₁₀ into CO₂ stream imply that solvent(s)-enriched CO₂ processes is a highly promising technique to recover heavy oil resources where other recovery techniques are not economically or efficiently available. Therefore, it is necessary to conduct the following experiments and possible pilot tests to determine the potential of applying variants of solvent(s)-enriched CO₂ processes for effective heavy-oil recovery purposes. Relevant research topics are recommended as follows.

1) The emergence of solid phase, i.e., asphaltene precipitation, is not elaborated in the present study, though it is also an important aspect of the phase behaviour of solvent(s)-CO₂-heavy oil systems. Asphaltene precipitation plays an important role in affecting the physical properties of solvent-diluted heavy oil and consequently the fluid flow in porous media. It is, therefore, necessary to conduct experiments to measure the onset and quantity of asphaltene precipitation in heavy oil when the heavy oil is diluted with solvent(s)-CO₂ mixtures. More accurate EOS-based thermodynamic model needs to be developed to well represent the experimental asphaltene-precipitation data considering the complexity of asphaltene precipitation phenomenon;
2) The importance of second-liquid phase in L1L2V behaviour of the solvent(s)-CO2-heavy oil systems needs further investigation and clarification since it may be inevitable to encounter formation of the second-liquid phase when injecting C3H8- or n-C4H10-enriched CO2 stream, in particular, with a high enrichment level, into heavy-oil reservoirs. Non-equilibrium mass transfer tests considering three phases, instead of only considering gas-heavy-oil two phases, might be able to reveal whether the occurrence of the second liquid-phase is beneficial for improving the mass transfer between solvent(s)-CO2 mixture and heavy oil. Well-designed coreflood experiments should also be conducted to shed lights on the effect of the second liquid-phase on the heavy-oil recovery efficiency;

3) As for the heavy oil recovery in various formations, different solvent(s)-CO2 injection methods could be evaluated both in laboratory experiments and possible pilot tests. Depending on the specific conditions of heavy oil reservoirs, the variants of these solvent(s)-enriched CO2 processes may include huff-n-puff method, continuous gas flooding, vapour extraction utilizing horizontal-well technology, and water-alternating-gas injection. In addition, in these processes, it is necessary to compare the performance of two generic injection methods: the injection of bulk solvent(s)-CO2 mixture and the cyclic injection of solvent(s) slugs and CO2 slugs; and

4) When implementing a solvent(s)-CO2-based process in a field, field-scale economic analysis must be carefully addressed in a comprehensive manner with the primary consideration of the large expenses associated with
purchasing solvent(s), recycling solvent(s), retrieving solvent(s) during production, and possible loss of unrecoverable rich solvent(s) that flee into thief zones or atmosphere.
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