

CHAPTER IV RESULTS AND DISCUSSION

4.1 Theoretical

4.1.1 The Onset Solubility Parameter Prediction

Wang, Buckley, and Creek (2004) proposed the empirical linear relationship between the onset solubility parameter (δ_{onset}) and the square root of precipitant molar volume ($v_p^{1/2}$) as illustrated in Figure 4.1.

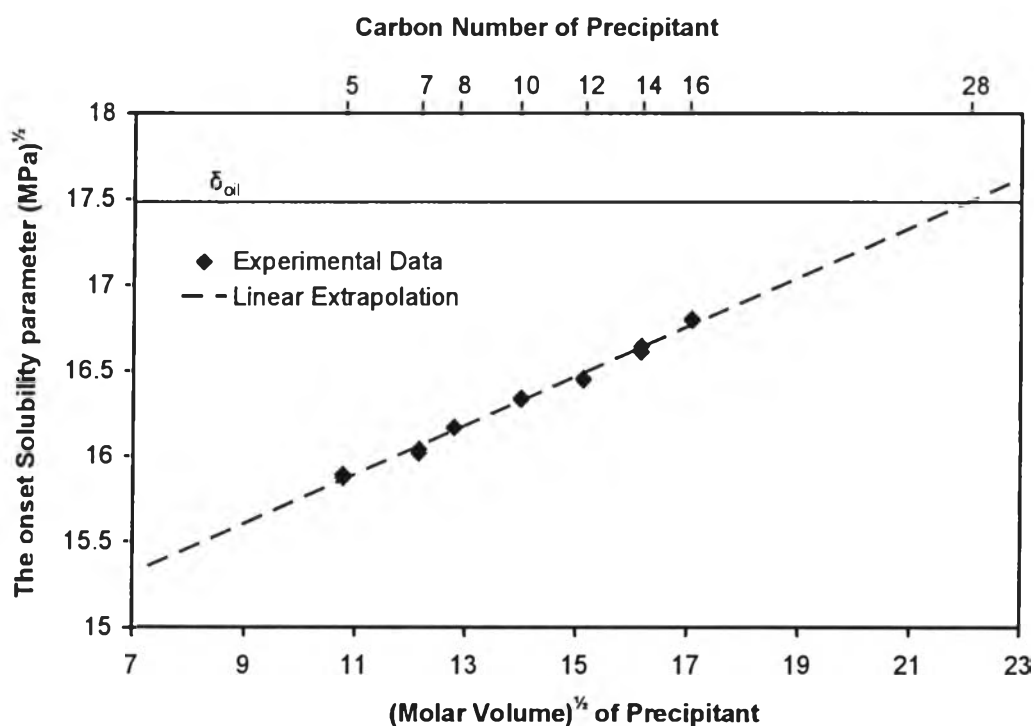


Figure 4.1 The onset solubility parameter as a function of square root of the molar volume of precipitant.

For the extrapolation of the higher molar volume of precipitant, the onset solubility parameter should never cross the oil solubility parameter (δ_{oil}). The crossing of the lines suggests that when the crude oil is mixed with the high molar volume precipitant or high molar volume crude oil, asphaltene precipitation would occur immediately, which is not valid. Understanding the theoretical background

helps determine the relationship between the onset solubility parameter and molar volume of precipitant.

From the Gibbs free energy of mixing equation;

$$\Delta G = \Delta H - T\Delta S \quad (4.1)$$

where ΔG = Gibbs free energy of mixing (J/mol)

ΔH = enthalpy of mixing (J/mol)

ΔS = entropy of mixing (J/K/mol)

The entropy and enthalpy terms can be estimated as a function of the solubility parameter (Hildebrand and Scott, 1964), the Gibbs free energy of mixing of asphaltene into the maltenes/precipitant mixture is shown:

$$\Delta G = v_a \phi_m^2 (\delta_a - \delta_m)^2 + RT \left[\ln \phi_a + \phi_m \left(1 - \frac{v_a}{v_m} \right) \right] \quad (4.2)$$

where ΔG = Gibbs free energy of mixing (J/mol)

v = molar volume (cm³/mol)

ϕ = volume fraction

δ = the solubility parameter (MPa)^{1/2}

R = gas constant (8.314 J/K/mol)

T = temperature (K)

Subscript a indicates the asphaltene phase and subscript m indicates the mixture phase rather than asphaltenes. At the equilibrium of asphaltene precipitation onset, the Gibbs free energy of mixing is zero and the solubility of the mixture can be estimated to be the onset solubility parameter. Fitting the experimental data to equation (4.2), the parameters v_a, δ_a can be obtained. The theoretical extrapolation is shown in Figure 4.2.

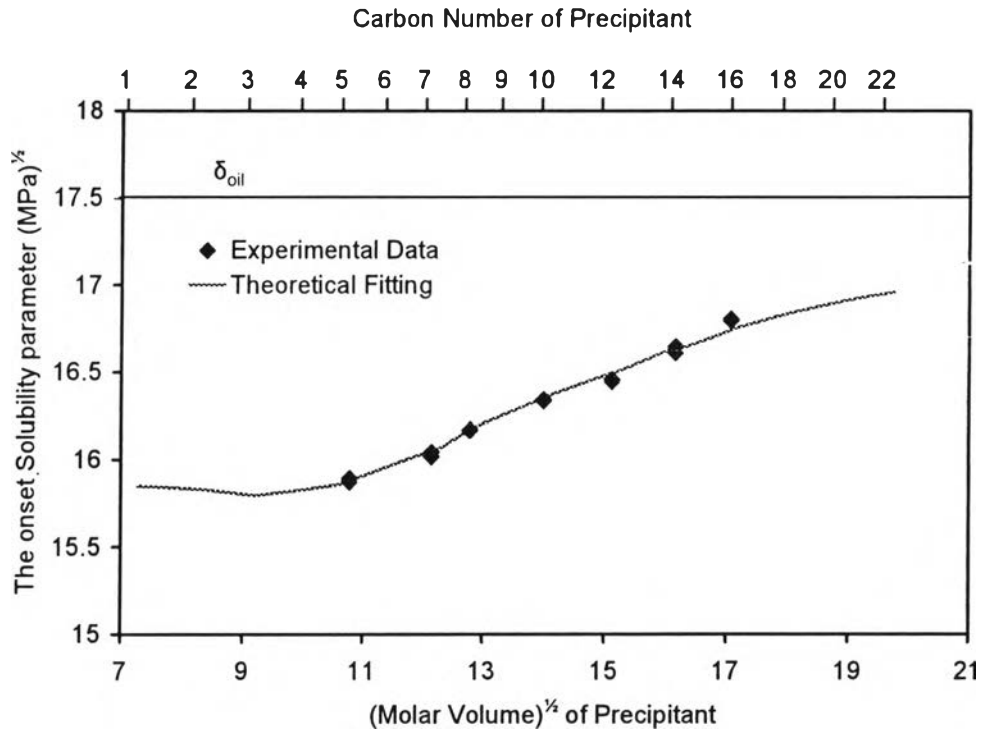


Figure 4.2 The onset solubility parameter (δ_{onset}) as a function of square root of molar volume of precipitant ($v_p^{1/2}$) fitting with the theoretical Gibbs free energy of mixing.

Equation (4.2) can also be rearranged to

$$\delta_{onset} = \delta_a - \left[\frac{RT/\phi_m}{v_m} - \frac{RT \ln \phi_a + RT \phi_m}{v_a \phi_m^2} \right]^{1/2} \quad (4.3)$$

Plotting the square root term of equation (4.3) with the square root of molar volume of the mixture ($v_m^{1/2}$), it shows a linear relationship within the range of v_m of interest in Figure 4.3.

From Figure 4.3 because it has a linear relationship, it can be implied that;

$$\left[\frac{RT/\phi_m}{v_m} - \frac{RT \ln \phi_a + RT \phi_m}{v_a \phi_m^2} \right]^{1/2} \cong A - Bv_m^{1/2} \quad (4.4)$$

From equations (4.3) and (4.4);

$$\delta_{onset} \cong \delta_a - A + Bv_m^{1/2} \quad (4.5)$$

Or
$$\delta_{onset} \cong A' + Bv_m^{1/2} \quad (4.6)$$

As a result, the onset solubility parameter is theoretically related to the square root of molar volume of the mixture as illustrated in Figure 4.4.

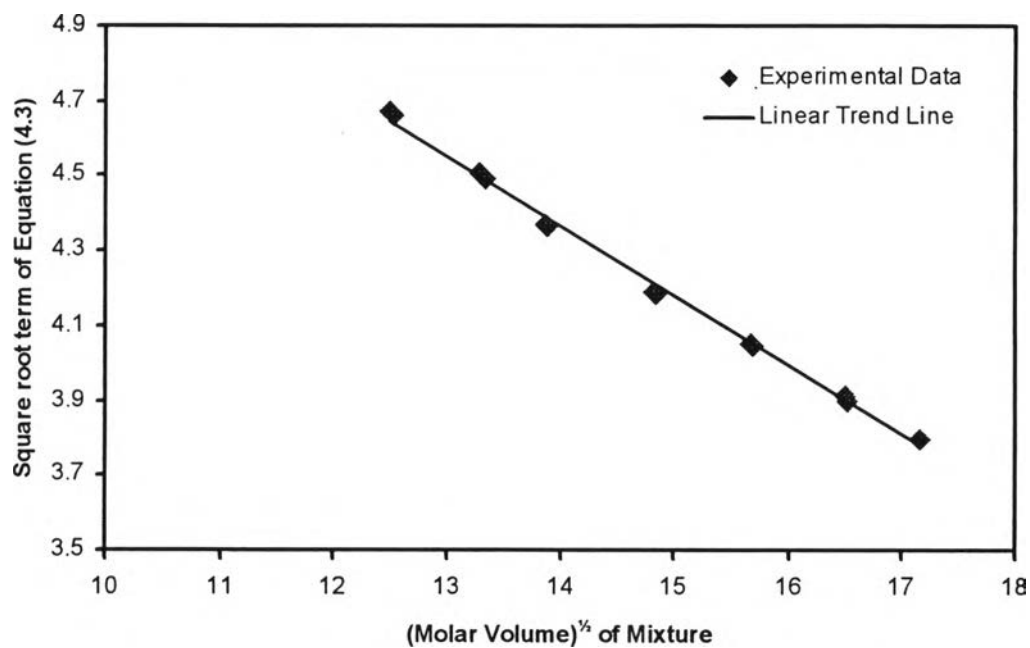


Figure 4.3 Square root term of equation (4.3) as a function of square root of molar volume of mixture ($v_m^{1/2}$).

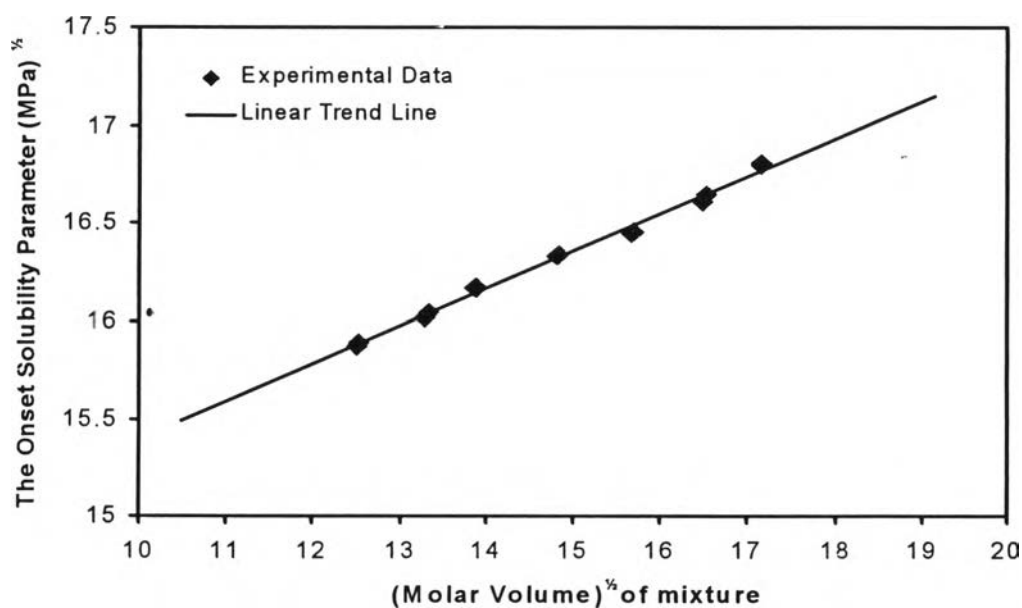


Figure 4.4 The onset solubility parameter (δ_{onset}) as a function of the square root of molar volume of the mixture ($v_m^{1/2}$).

For simplicity of the onset solubility parameter prediction, using this molar volume of the mixture and the onset solubility parameter relationship gave the right extrapolation based on Gibbs free energy of mixing for the higher molar volume and lower molar volume precipitant. Figure 4.5 shows a comparison between the linear extrapolation, the extrapolation with Gibbs free energy of mixing fitting, and the extrapolation with the square root of molar volume of the mixture ($v_m^{1/2}$).

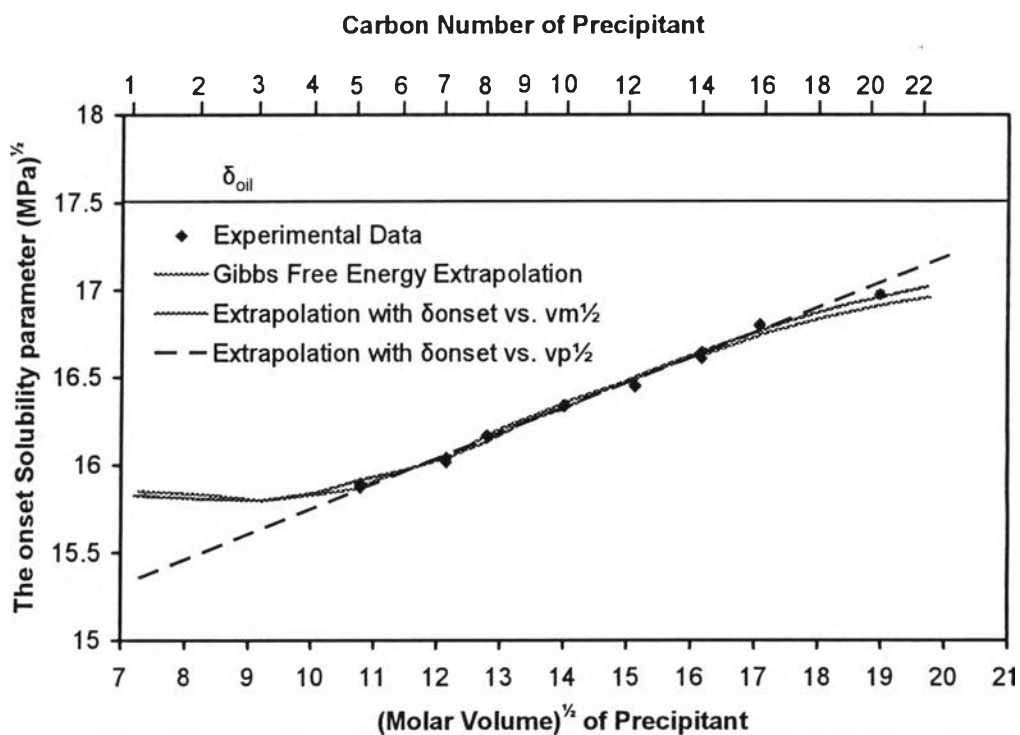


Figure 4.5 The comparison among the linear extrapolation, the extrapolation with the Gibbs free energy of mixing fitting, and the extrapolation with the square root of molar volume of the mixture ($v_m^{1/2}$).

The graph shows that the extrapolation with the square root of molar volume of the mixture ($v_m^{1/2}$) fits with the theory in the range of 7-19. For the higher precipitant molar volumes, the linear extrapolation overestimates the onset solubility parameter, while lower precipitant molar volumes; the linear extrapolation underestimates the onset solubility parameter.

The extrapolation from the Gibbs free energy of mixing equation was then used to predict the onset solubility parameter for reservoir conditions. Knowing

the onset solubility parameter (δ_{onset}) as a function of the square root of molar volume of the mixture ($v_m^{1/2}$) at 2 or 3 temperatures allows for the onset solubility parameter to be predicted at any conditions. Figure 4.6 shows the onset solubility parameter (δ_{onset}) as a function of the square root of molar volume of the mixture ($v_m^{1/2}$) at different temperatures.

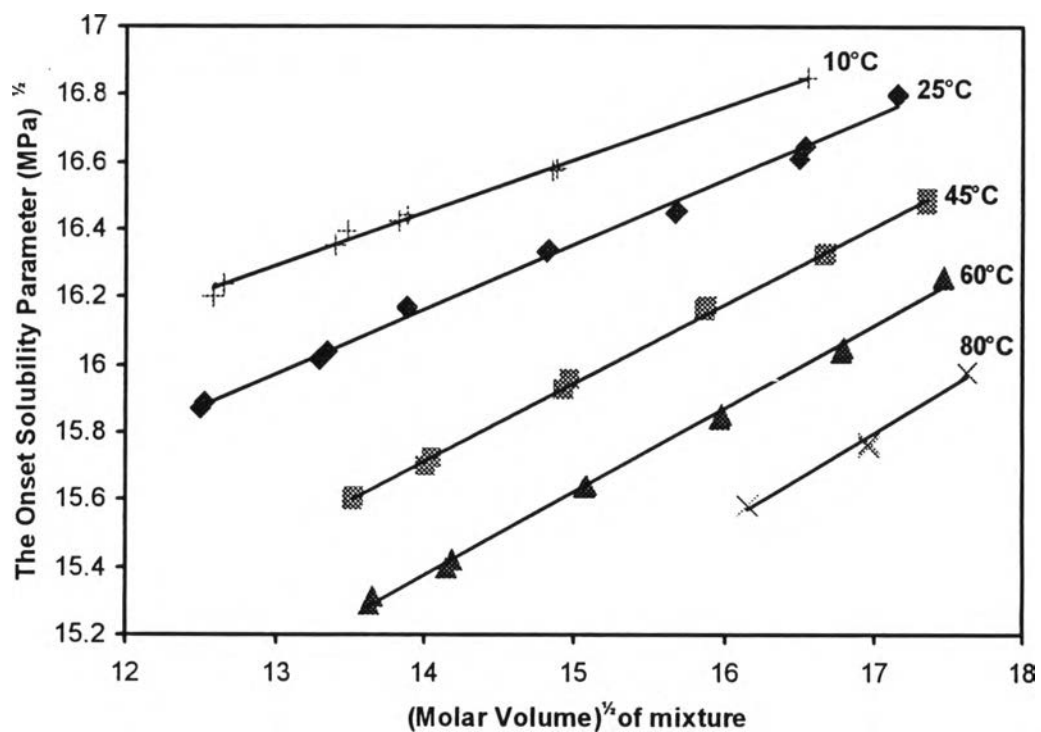


Figure 4.6 The onset solubility parameter (δ_{onset}) as a function of the square root of molar volume of the mixture ($v_m^{1/2}$) at different temperature.

4.2 Mathematical Model

The objective of the mathematical model is to predict the asphaltene precipitation in the live oil at reservoir condition or any process condition with or without miscible injection from the experimental data and the EOS data from a PVT simulator.

4.2.1 The Live Oil Solubility Parameter Calculation

The live oil can be considered as a mixture of stock tank oil and dissolved gas. Since the solubility parameter obeys the volume average mixing rule, the live oil solubility parameter (δ_{LO}) can be expressed as:

$$\delta_{LO} = \phi_{STO} \delta_{STO} + \phi_{DG} \delta_{DG} \quad (4.7)$$

where δ_{STO} = solubility parameter of stock tank oil (MPa)^{1/2}

δ_{DG} = solubility parameter of dissolved gas (MPa)^{1/2}

ϕ_{STO} = volume fraction of stock tank oil

ϕ_{DG} = volume fraction of dissolved gas

Equation (4.4) can be expressed in terms of the molar solubility parameter of dissolved gas (δ_{DG}^M) as follows:

$$\delta_{LO} = \frac{1}{B} \delta_{STO} + \frac{R}{B} \delta_{DG}^M \quad (4.8)$$

where B = volume ratio of the live oil to the stock tank oil at live oil conditions

R = ratio of moles of dissolved gas to ml of stock tank oil at live oil conditions

The parameters B and R can be calculated from a flash calculation of the live oil to the stock tank condition, and δ_{DG}^M is calculated from the flashed gas composition using equation (2.6).

Values of B and R are shown in Figure 4.7 and the volume fraction of dissolved gas is shown in Figure 4.8.

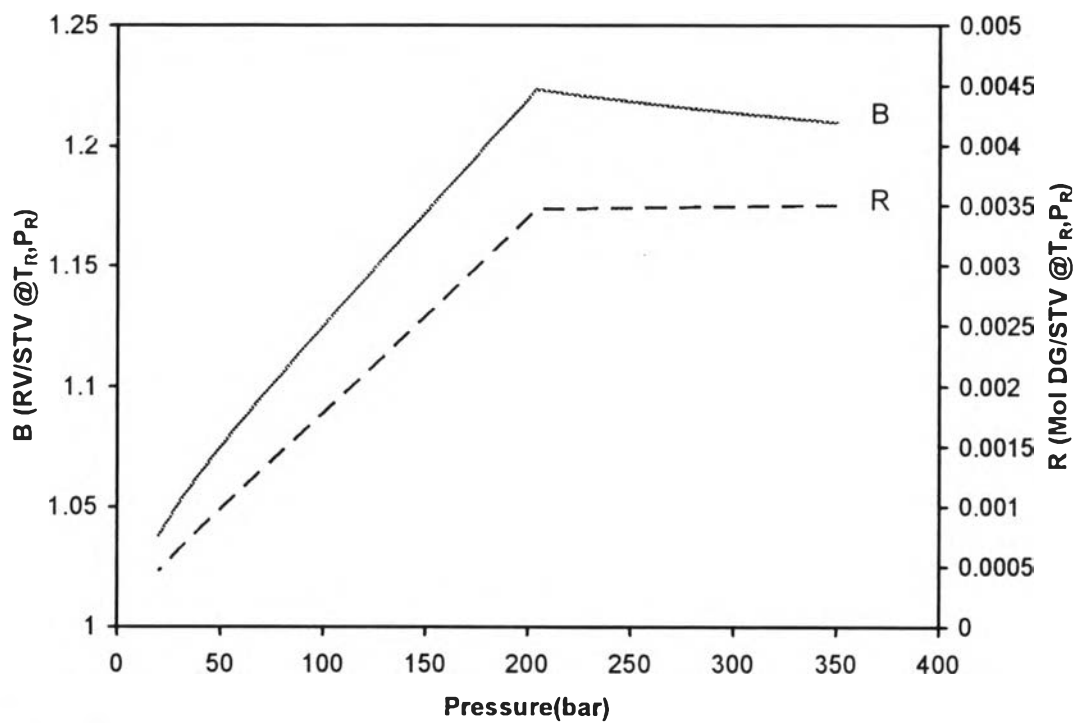


Figure 4.7 Values of B and R at different pressures.

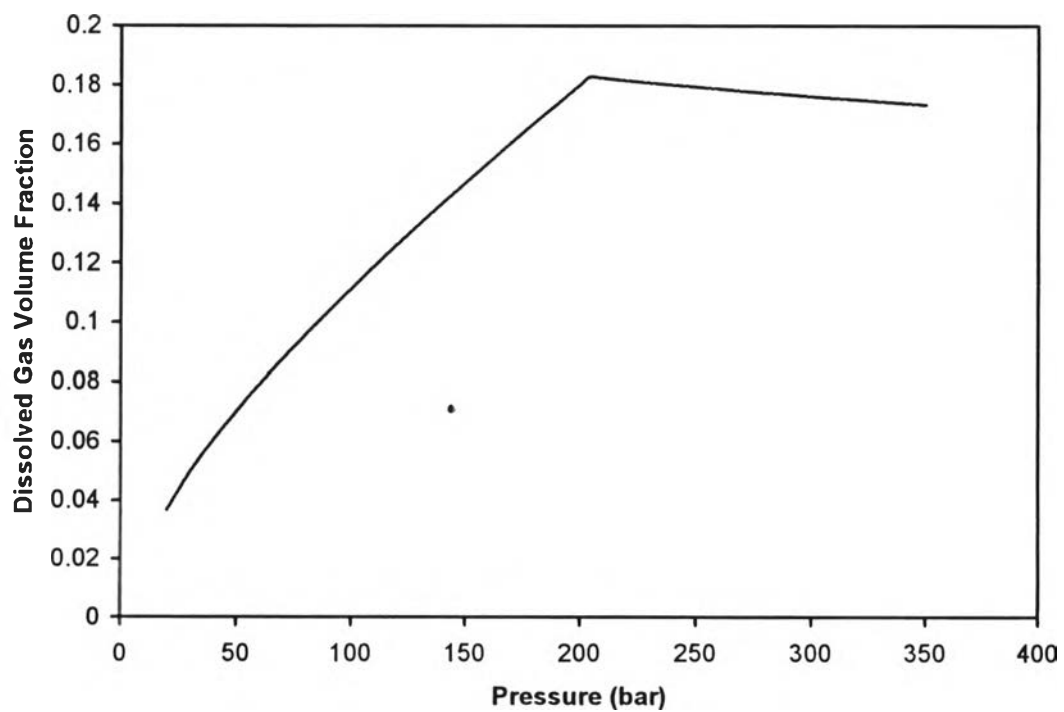


Figure 4.8 Dissolved gas volume fraction as a function of pressure.

From Figures 4.7 and 4.8, as the pressure decreases from 350 bar (above the bubble point) to the bubble point pressure, the dissolved gas (mostly normal alkanes) expands more than the stock tank oil. Therefore, the dissolved gas volume fraction and value of B increase. But the moles of gas dissolved in liquid phase are the same causing R to decrease because of volume expansion of stock tank oil. After the pressure reaches the bubble point, the dissolved gas evaporates from the liquid phase, and thus B , R and dissolved gas volume fraction all decrease.

The stock tank oil solubility parameter at reservoir conditions can be estimated from the experimental data at ambient conditions using equations (2.3) and (2.4) with $n = 1.25$.

However, in order to more accurately predict the stock tank oil solubility parameter, the stock tank oil solubility parameter at different temperatures may be needed to determine the exact value of n . The experimental results of the stock tank oil solubility parameter as a function of molar volume are shown in Figure 4.9.

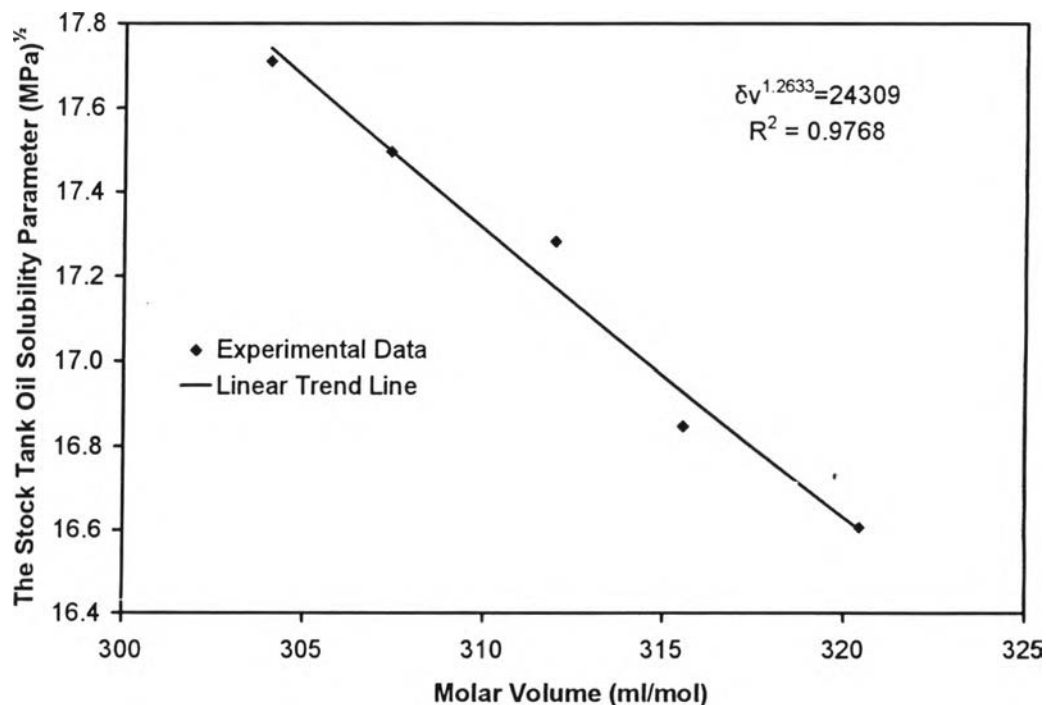


Figure 4.9 The stock tank oil solubility parameter (δ_{STO}) as a function of molar volume.

Then the stock tank oil solubility parameter at any condition can be calculated from the equation in Figure 4.9 by interpolation or extrapolation.

The live oil solubility parameter was calculated using equation (4.8) and the result is shown with the onset solubility parameter as in Figure 4.10.

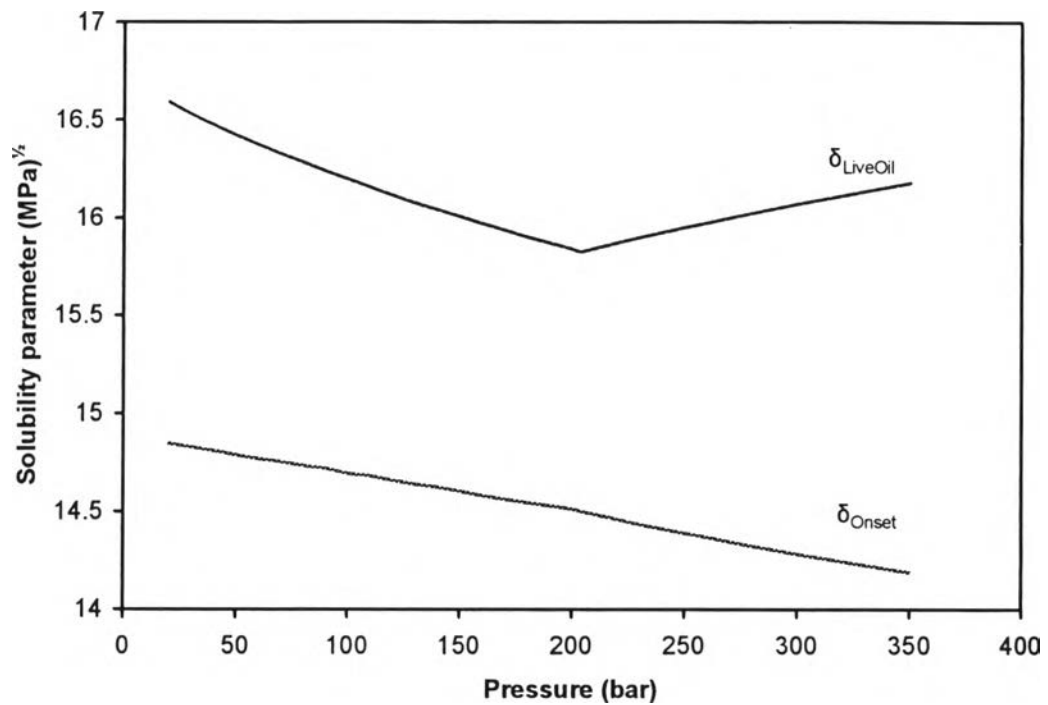


Figure 4.10 The live oil solubility parameter (δ_{LO}) and the onset solubility parameter (δ_{onset}) as a function of temperature.

From Figure 4.10., if the live oil solubility parameter is lower than the onset solubility parameter, asphaltene precipitation will occur.

4.3 Field Application

4.3.1 Oil A

The Oil A field is located in North Slope, Alaska. Currently, it produces 200,000 BOPD of 22-24 API Gravity oil. Miscible Injection (MI) of 300 MMSCFD and water-reinjected produced water/sea water mix of 670,000 barrels of water per day (BWPD) are used to enhance the oil recovery.

The composition of Oil A live oil, dissolved gas, and stock tank oil is shown in Table 4.1.

Table 4.1 Composition of Oil A live oil, dissolved gas, and stock tank oil

Hydrocarbon	Live oil (mol%)	Dissolved gas (mol%)	Stock Tank Oil (mol%)
CO ₂	0.512	0.984	0.000
C ₁	42.094	80.864	0.000
C ₂	3.921	7.532	0.000
C ₃	2.772	5.325	0.000
C ₄	2.095	2.760	1.373
C ₅	1.151	0.820	1.510
C ₆ C ₇	2.891	1.434	4.472
C ₈ C ₁₀	7.936	0.277	16.251
C ₁₁ C ₁₄	10.361	0.005	21.606
C ₁₅ C ₁₉	9.332	0.000	19.464
C ₂₀ C ₂₉	8.932	0.000	18.629
C ₃₀ +	8.004	0.000	16.695

The experimental results show that the asphaltenes in Oil A stock tank oil are quite stable in the experimental range (difference of the oil solubility parameter and the onset solubility parameter is about 1 MPa^{1/2}). The oil solubility parameter of Oil A at different temperatures is shown in Figure 4.11 and the onset solubility parameter of Oil A titrated with different normal alkanes at different

temperatures plotting with the square root of molar volume of the precipitant is shown in Figure 4.12.

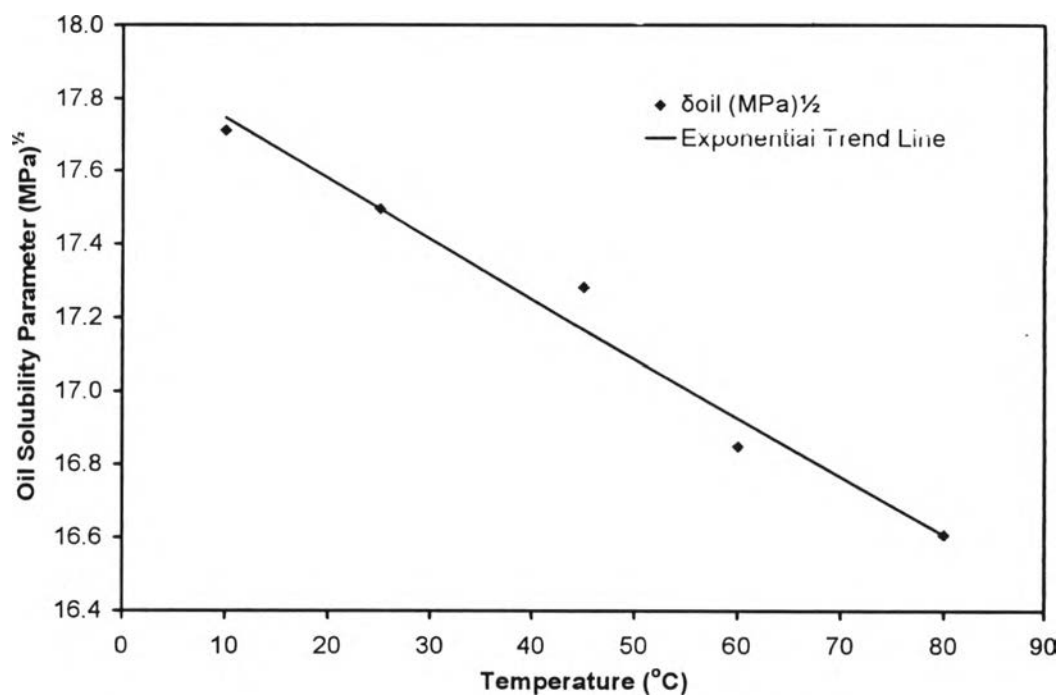


Figure 4.11 The oil solubility parameter of Oil A at different temperatures

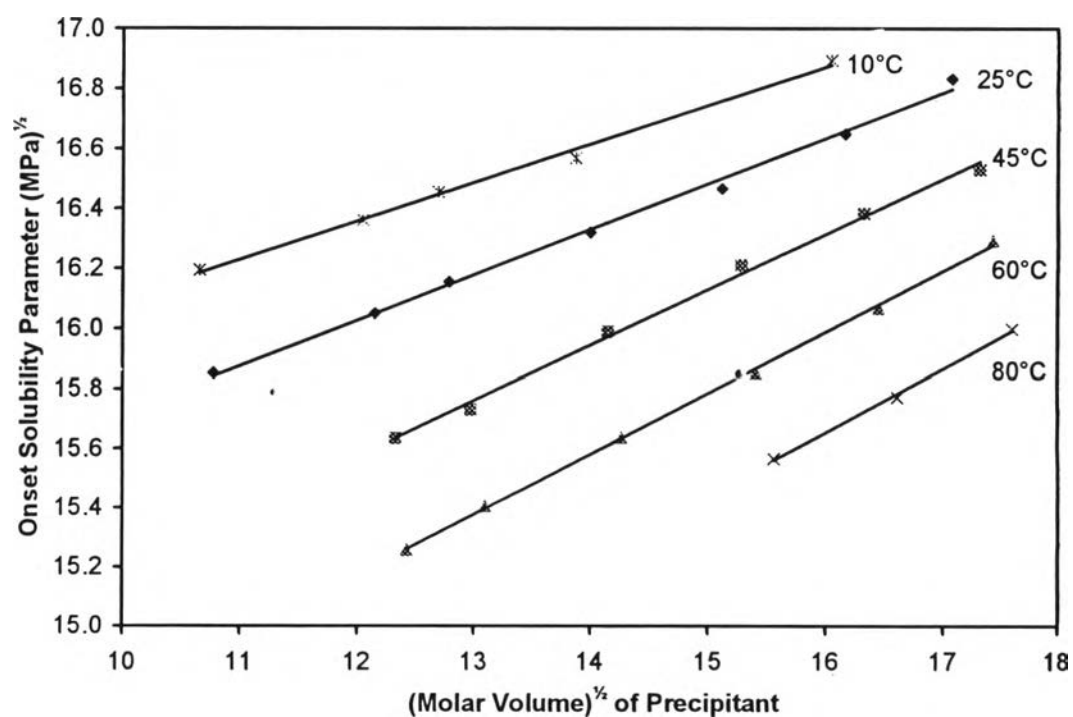


Figure 4.12 The onset solubility parameter of Oil A titrated with different normal

alkanes at different temperatures plotting with the square root of molar volume of the precipitant.

From the theory, the onset solubility parameter at reservoir conditions can be predicted from the relationship between the onset solubility parameter and the square root of molar volume of the mixture as shown in Figure 4.13.

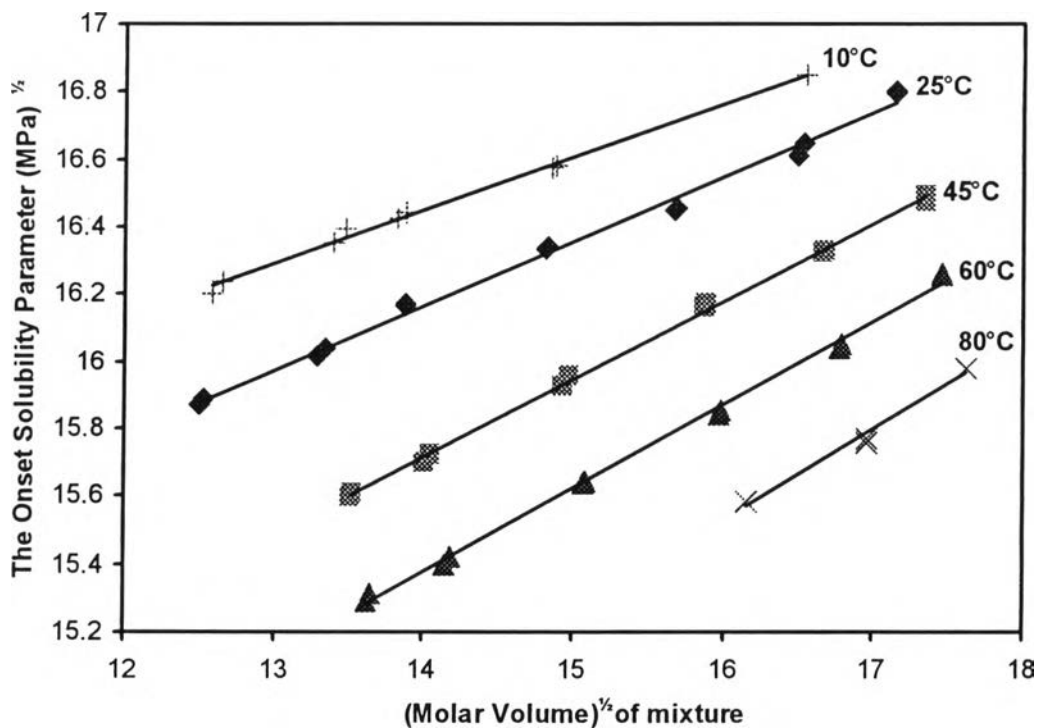


Figure 4.13 The onset solubility parameter of Oil A titrated with different normal alkanes at different temperatures plotting with the square root of molar volume of the mixture.

The results of the prediction for the reservoir conditions show that the live oil solubility parameter is always higher than the onset solubility parameter or the live oil is stable during depressurization as shown in Figure 4.14.

Due to the usage of miscible injection (mostly light normal alkanes) to enhance the oil recovery, the effect of miscible injectant was studied. The composition of the miscible injectant for Oil A is shown in Table 4.2.

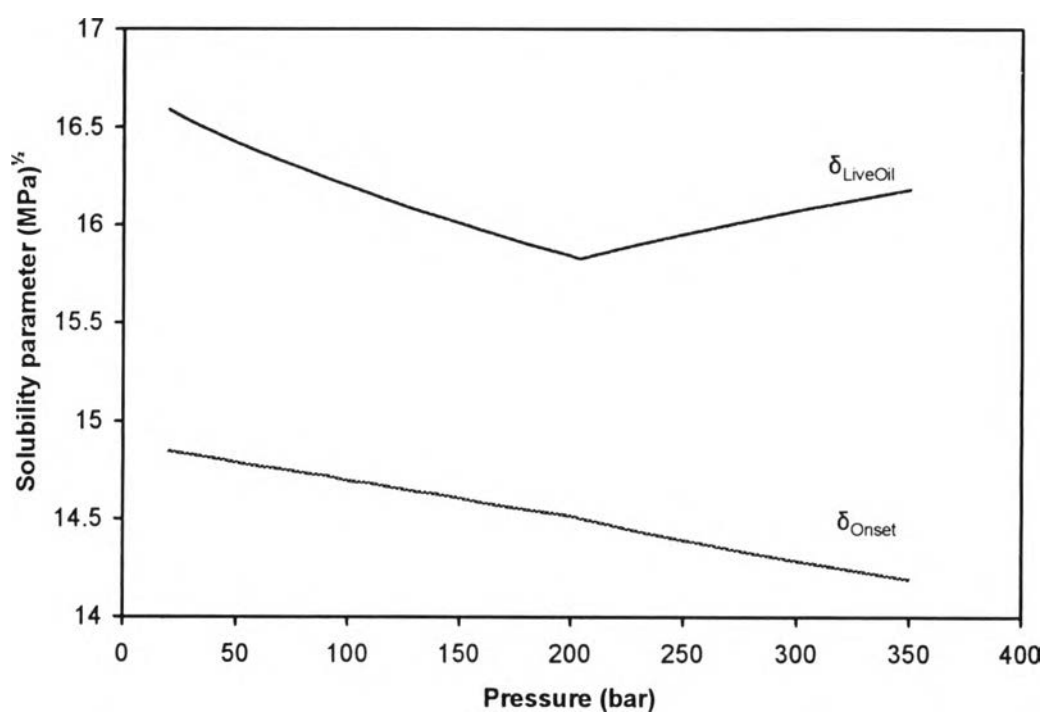


Figure 4.14 The live oil solubility parameter and the onset solubility parameter prediction of Oil A at reservoir temperature (160°F) during depressurization.

Table 4.2 Composition of miscible injectant for Oil A field

Hydrocarbon	Composition (mol%)
CO ₂	0.55
C ₁	69.88
C ₂	6.69
C ₃	5.13
C ₄	8.39
C ₅	4.43
C ₆ C ₇	3.87
C ₈ C ₁₀	1.01
C ₁₁ C ₁₄	0.05
C ₁₅ C ₁₉	0
C ₂₀ C ₂₉	0
C ₃₀ +	0

The live oil solubility parameter is lowered with higher percent miscible injectants because more miscible injectant dissolved into the live oil. But for the onset solubility parameter, miscible injectant contains almost the same composition as dissolved gas in the live oil therefore it gives almost the same onset solubility parameter.

The results show that injection of miscible injectant up to 60 mole% (22.4 wt.%) will not initiate any asphaltene precipitation at any pressure as shown in Figure 4.15.

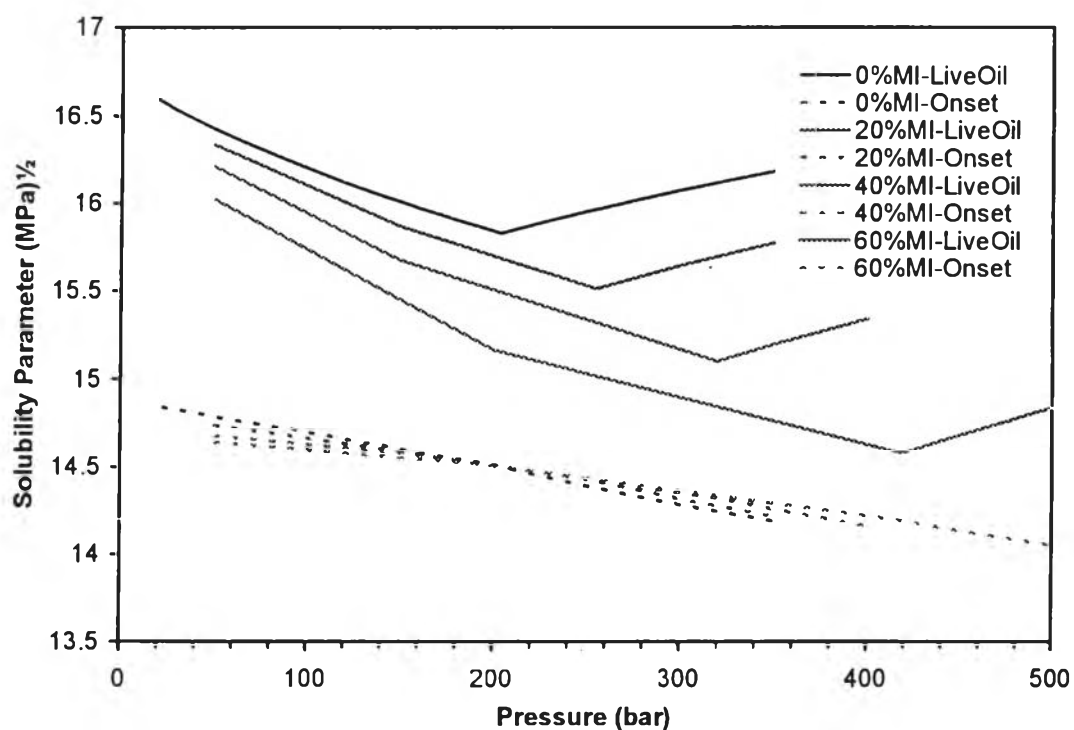


Figure 4.15 The live oil solubility parameter and the onset solubility parameter prediction of Oil A with different ratios of miscible injectant added.

And in the case that carbon dioxide is used instead of miscible injectant to enhance the oil recovery, it shows that carbon dioxide has less effect on the asphaltene stability. Due to the equilibrium of the gas phase and the liquid phase, carbon dioxide dissolved into the live oil while light hydrocarbon gases were chased out of the live oil. As a result, the live oil solubility parameter is slightly changed with higher percent carbon dioxide injected but the onset solubility parameter

changed due to the change in the dissolved gas component in the liquid phase. The results in Figure 4.16 show that there will be no asphaltene precipitation problem at all. However, carbon dioxide is corrosive to the metal pipe; this issue has to be studied.

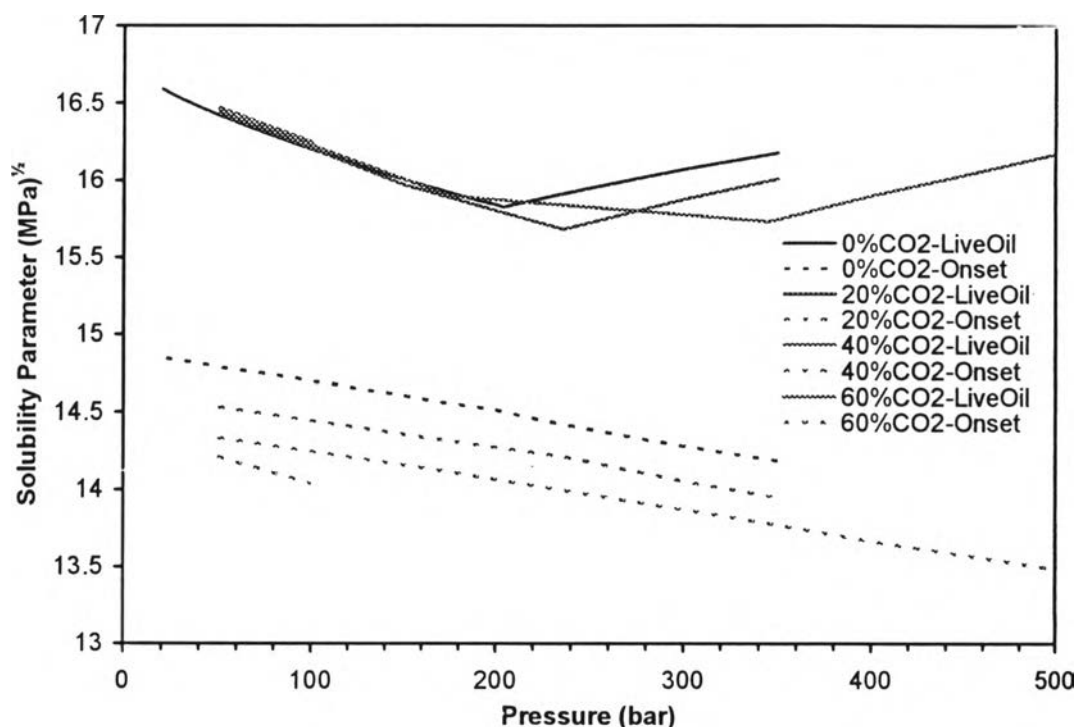


Figure 4.16 The live oil solubility parameter and the onset solubility parameter prediction of Oil A with different ratios of carbon dioxide added.

4.3.2 Oil B

The Oil B field was discovered in 1999 at a depth of 6,900 with 37 million barrels OOIP (30 API gravity). The Oil B field is a satellite production in North Slope, Alaska. The composition of Oil B live oil, dissolved gas, and stock tank oil is shown in Table 4.3.

Table 4.3 Composition of Oil B live oil, dissolved gas, and stock tank oil

Hydrocarbon	Live oil (mol%)	Dissolved gas (mol%)	Stock Tank Oil (mol%)
N ₂	0.411	0.782	0.000
CO ₂	0.32	0.608	0.000
C ₁	36.474	69.341	0.000
C ₂	4.386	8.338	0.000
C ₃	5.691	10.820	0.000
C ₄	4.538	5.986	2.931
C ₅	3.212	2.290	4.235
C ₆	3.749	1.198	6.580
C ₇ C ₈	7.497	0.557	15.198
C ₉ C ₁₀	5.889	0.072	12.344
C ₁₁ C ₁₃	6.414	0.007	13.524
C ₁₀ +	21.419	0.001	45.188

The experimental results show that the asphaltenes in Oil B stock tank oil are stable, but less stable than Oil A. The oil solubility parameter of Oil B at different temperatures is shown in Figure 4.17 and the onset solubility parameter of Oil B titrated with different normal alkanes at different temperatures plotting with the square root of molar volume of the precipitant is shown in Figure 4.18.

From the theory, the onset solubility parameter at reservoir conditions can be predicted from the relationship between the onset solubility parameter and the square root of molar volume of the mixture as shown in Figure 4.19.

- The results of the prediction for the reservoir conditions show that the live oil solubility parameter of Oil B is always higher than the onset solubility parameter or the live oil is stable during depressurization as shown in Figure 4.20.

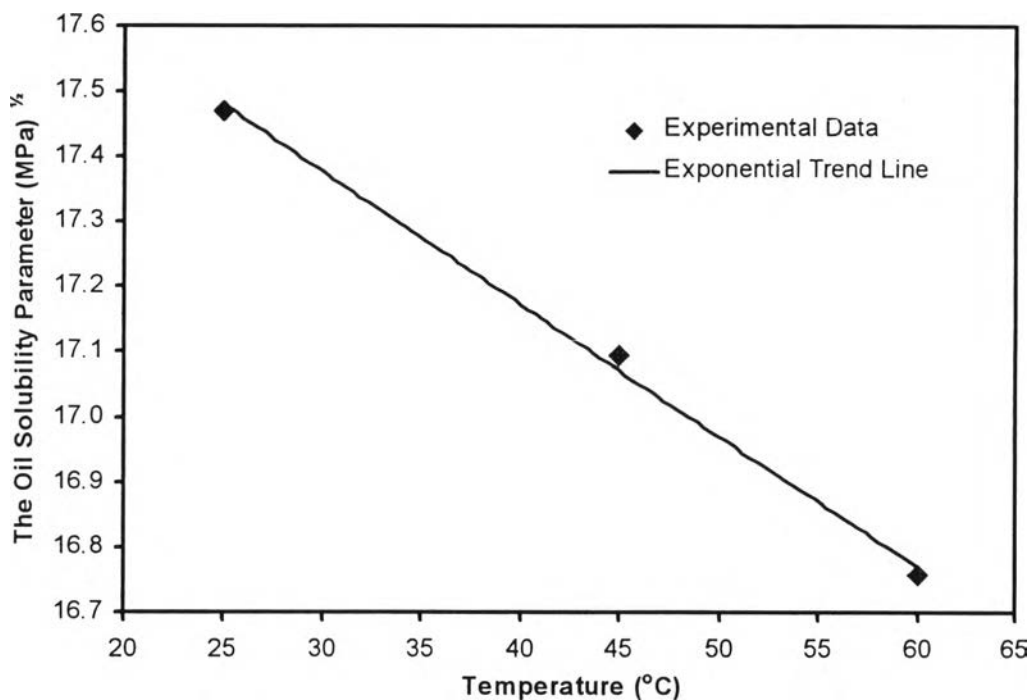


Figure 4.17 The oil solubility parameter of Oil B at different temperatures.

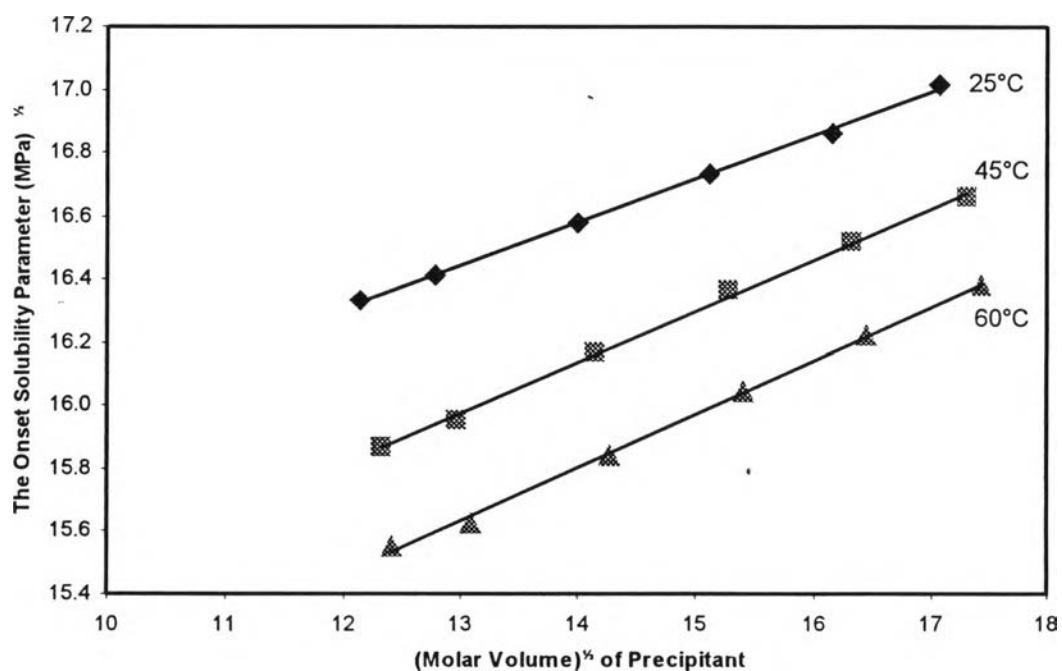


Figure 4.18 The onset solubility parameter of Oil B titrated with different normal alkanes at different temperatures plotting with the square root of molar volume of the precipitant.

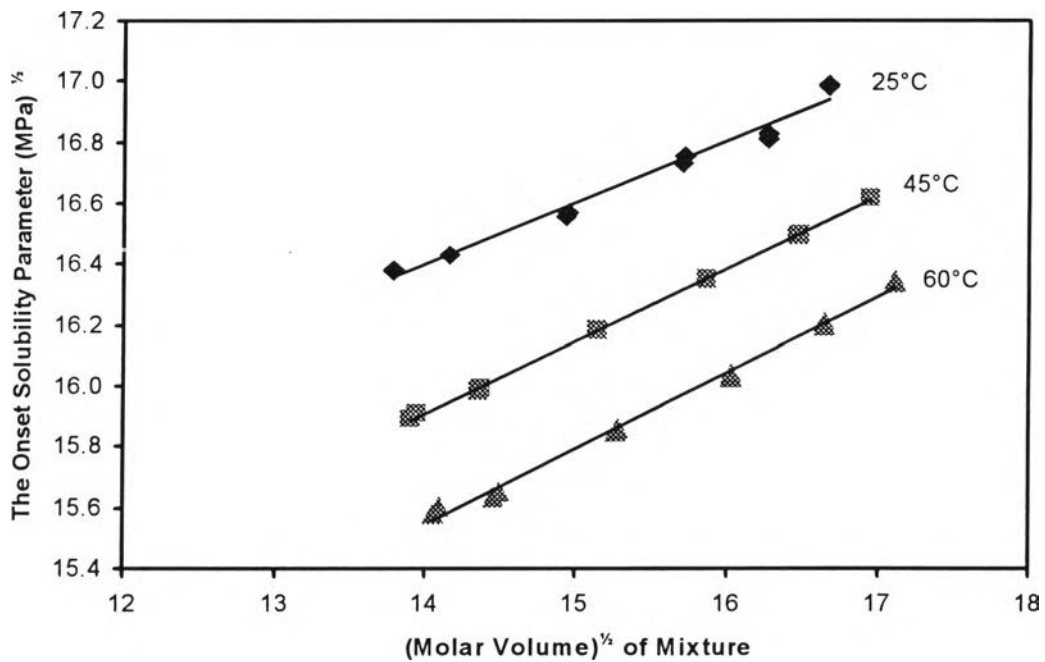


Figure 4.19 The onset solubility parameter of Oil B titrated with different normal alkanes at different temperatures plotting with the square root of molar volume of the mixture.

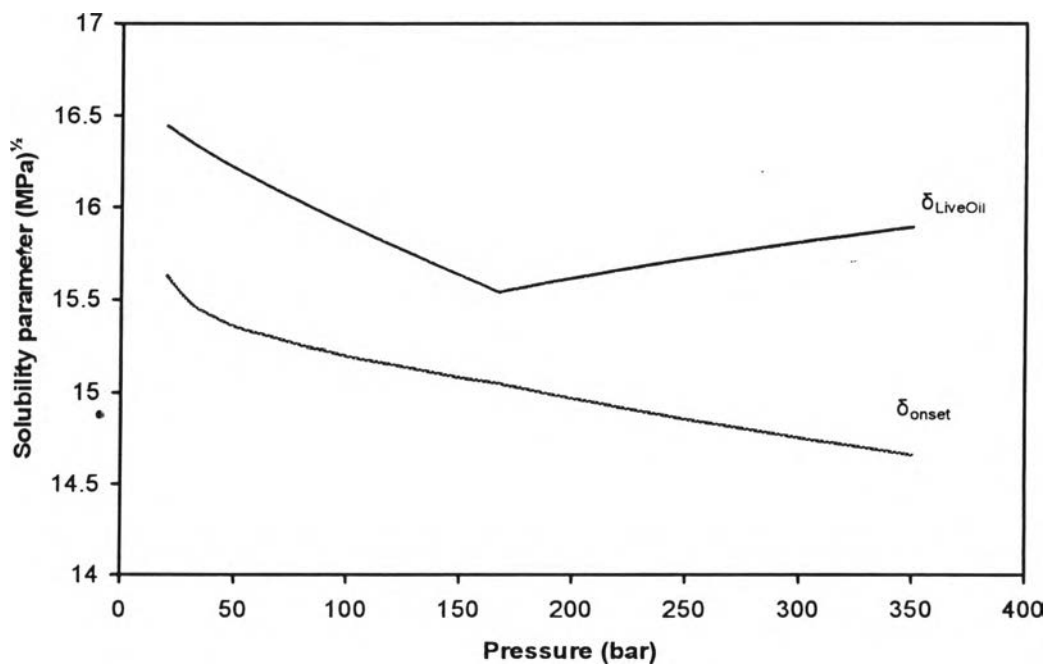


Figure 4.20 The live oil solubility parameter and the onset solubility parameter prediction of Oil B at reservoir temperature (165°F) during depressurization.

Since the use of miscible injectant is planned for the Oil B field to increase the oil recovery, the effect of miscible injectant to the asphaltene stability was studied. The composition of miscible injectant for Oil B is shown in Table 4.4.

Table 4.4 Composition of miscible injectant for Oil B field

Hydrocarbon	Composition (mol%)
N ₂	0.65
CO ₂	0.45
C ₁	62.936
C ₂	10.751
C ₃	14.331
C ₄	7.681
C ₅	2.18
C ₆	0.54
C ₇ C ₈	0.48
C ₉ C ₁₀	0
C ₁₁ C ₁₃	0
C ₁₀ +	0

Figure 4.21 shows that with 20 mole% miscible injectant, there will be no asphaltene precipitation problem, but there will be a problem at about 40 mole% (12.33 wt.%) miscible injectant at reservoir condition (214 bar). Therefore, based on interpolation between the 20 mole% miscible injectant and 40 mole% miscible injectant data, less than 30 mole% miscible injectant is preferred to keep asphaltene soluble in the live oil.

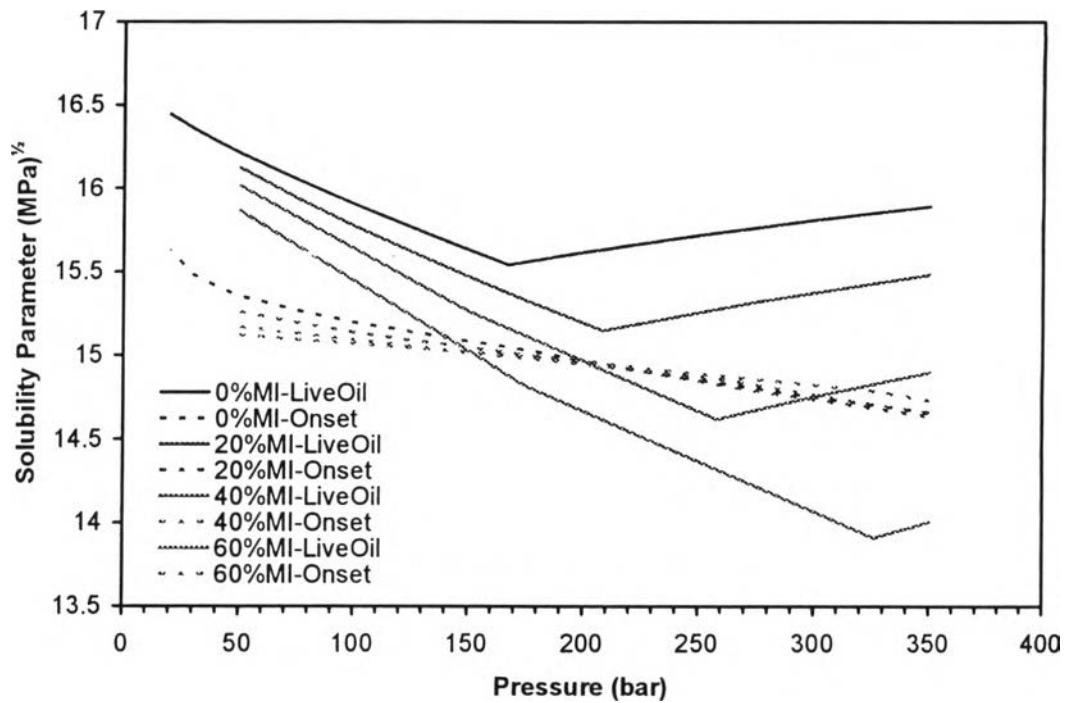


Figure 4.21 The live oil solubility parameter and the onset solubility parameter prediction of Oil B with different ratios of miscible injectant added.

A crude oil swell experiment for Oil B was performed by ConocoPhillips by adding different amounts of miscible injectant to the live oil in the high pressure and high temperature cell. The cell was pressured to 7,000 psi (480 bar) and then depressurized discretely from 7,000 psi (480 bar) to about 1,000 psi (70 bar). Asphaltene deposit at the cell wall was observed and then disappeared when the pressure was lowered further. The live oil solubility parameter and the onset solubility parameter prediction of the same ratio of miscible injectant with the experimental results are shown in Figure 4.22.

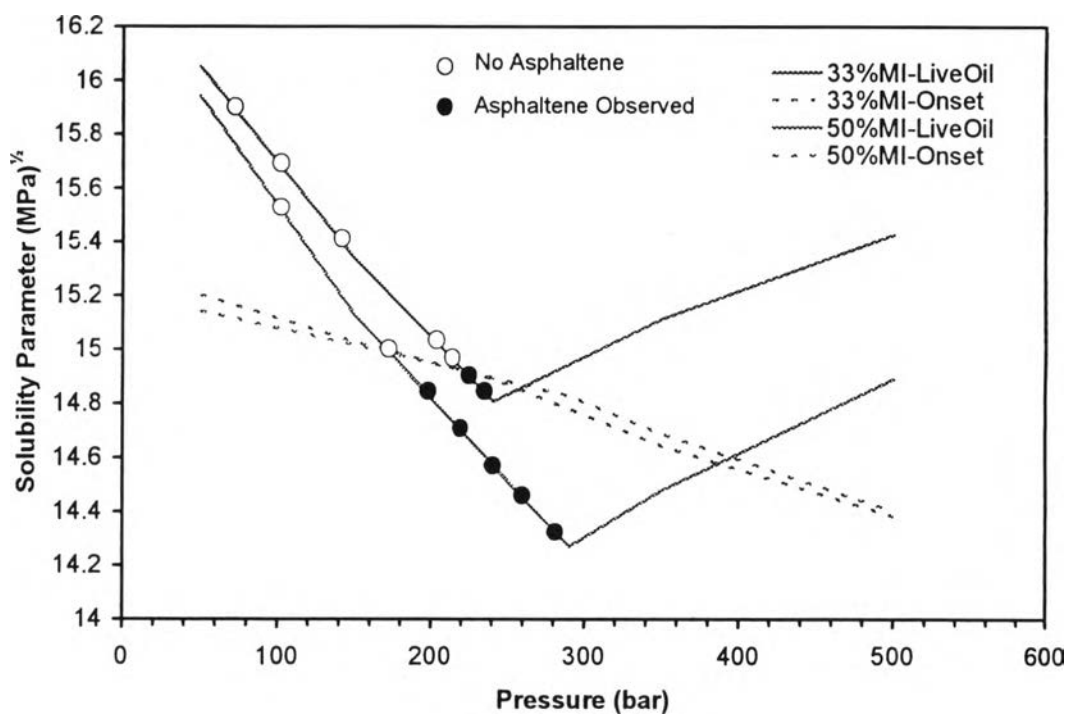


Figure 4.22 The comparison of the model prediction and experimental results of Oil B in the crude swell tests.

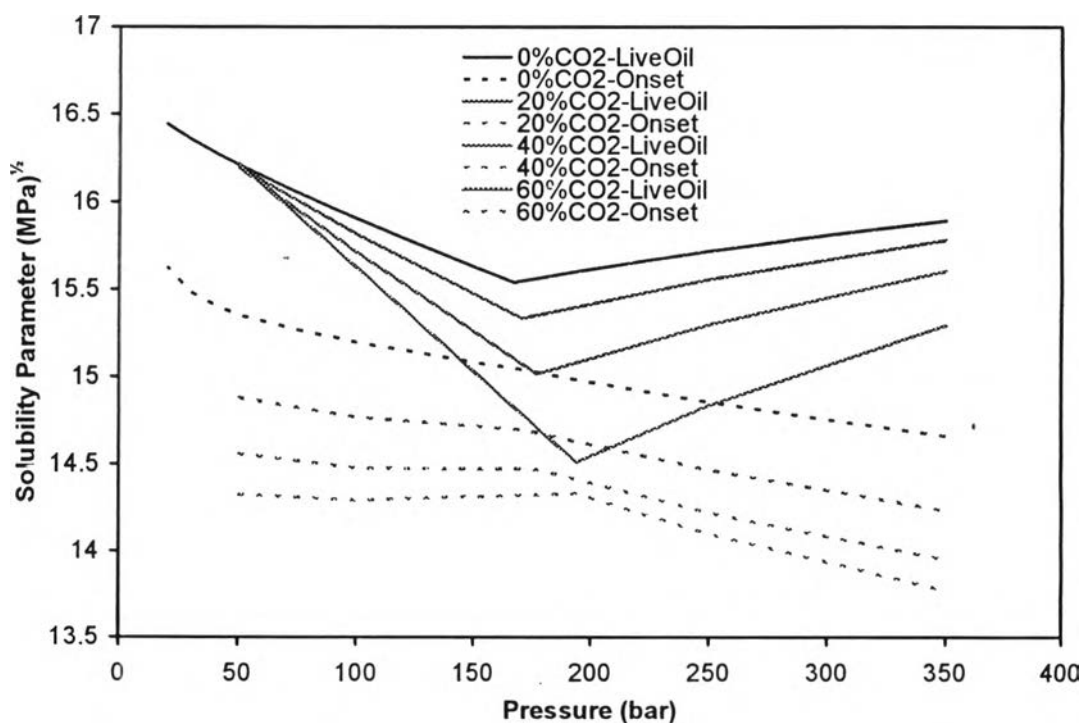


Figure 4.23 The live oil solubility parameter and the onset solubility parameter prediction of Oil B with different ratios of carbon dioxide added.

In the case of carbon dioxide injection to enhance the oil recovery, the results in Figure 4.23 show that there will be no asphaltene precipitation problem up to about 70 mole% carbon dioxide. Because carbon dioxide is less aggressive than methane (the most abundant component of miscible injectants) and due to the equilibrium between gas phase and liquid phase, carbon dioxide will replace methane in the liquid phase and make the live oil more stable.

4.3.3 Oil C

The Oil C field is located in northern Alberta with the produced bitumen being 7 to 8 API gravity and in the reservoir ($\sim 10^{\circ}\text{C}$) has a viscosity about 1,000,000 cP. Therefore, the significant viscosity reduction is required to increase the production rate and recovery.

Steam injection is currently used to reduce the viscosity of the bitumen. The operating conditions of the Oil C field are at 500 psi (34 bar) and 240°C . The composition of Oil C heavy oil is shown in Table 4.5.

Table 4.5 Composition of Oil C heavy oil

Hydrocarbon	Composition (mol%)
C11-C18	20.853
C19-C22	15.948
C23-C26	13.310
C27-C29	8.898
C30-C34	8.970
C35-C40	8.112
C41-C46	6.478
C47-C52	5.234
C53-C60	3.205
C61-C72	3.143
C73-C88	2.326
C89-C100	3.522

Even though the asphaltene content in the Oil C stock tank oil is very high (21.4 wt. %), the asphaltene are still soluble in liquid phase because of the high solubility of the Oil C itself. The experimental result indicates that the oil solubility parameter of Oil C is almost the same as toluene at any temperature as shown in Figure 4.24 and the onset solubility parameter is quite low compared to the oil solubility parameter (more than one $\text{MPa}^{1/2}$ different) as shown in Figure 4.25.

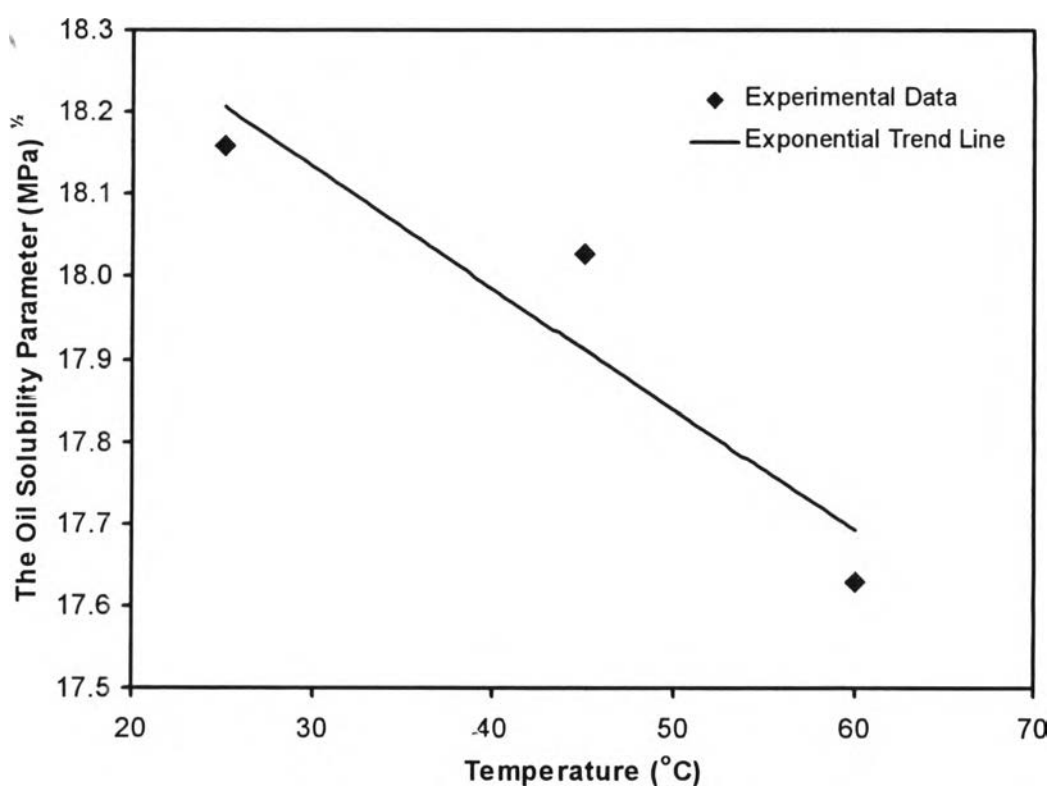


Figure 4.24 The oil solubility parameter of Oil C heavy oil at different temperatures.

From theory, the onset solubility parameter at reservoir conditions can be predicted from the relationship between the onset solubility parameter and the square root of molar volume of the mixture as shown in Figure 4.26.

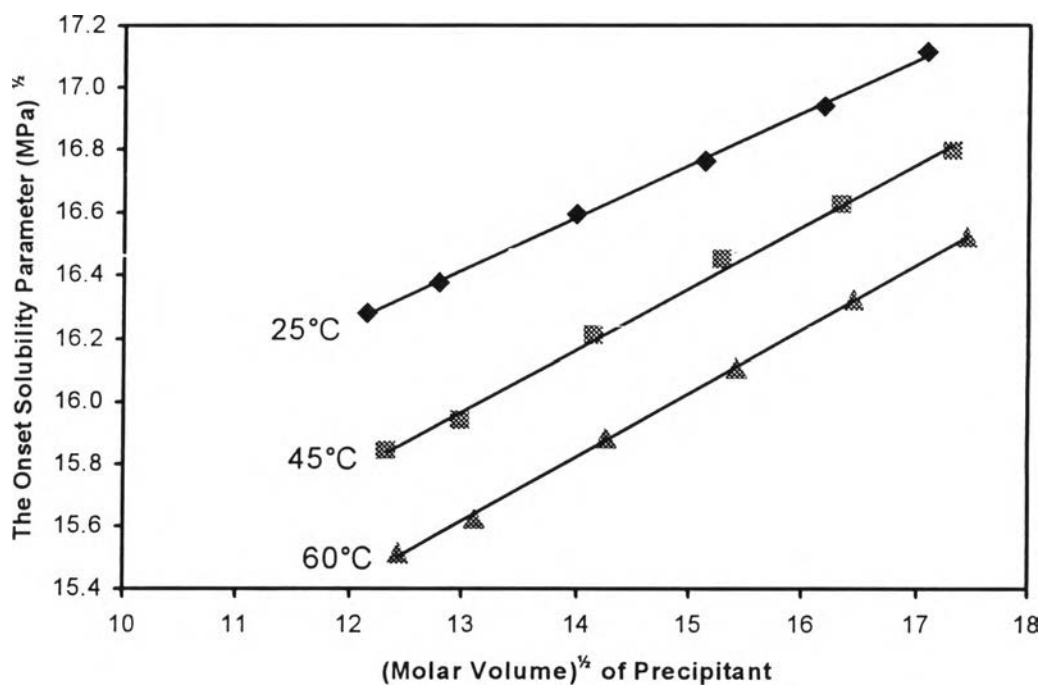


Figure 4.25 The onset solubility parameter of Oil C heavy oil titrated with different normal alkanes at different temperatures plotting with the square root of molar volume of the precipitant.

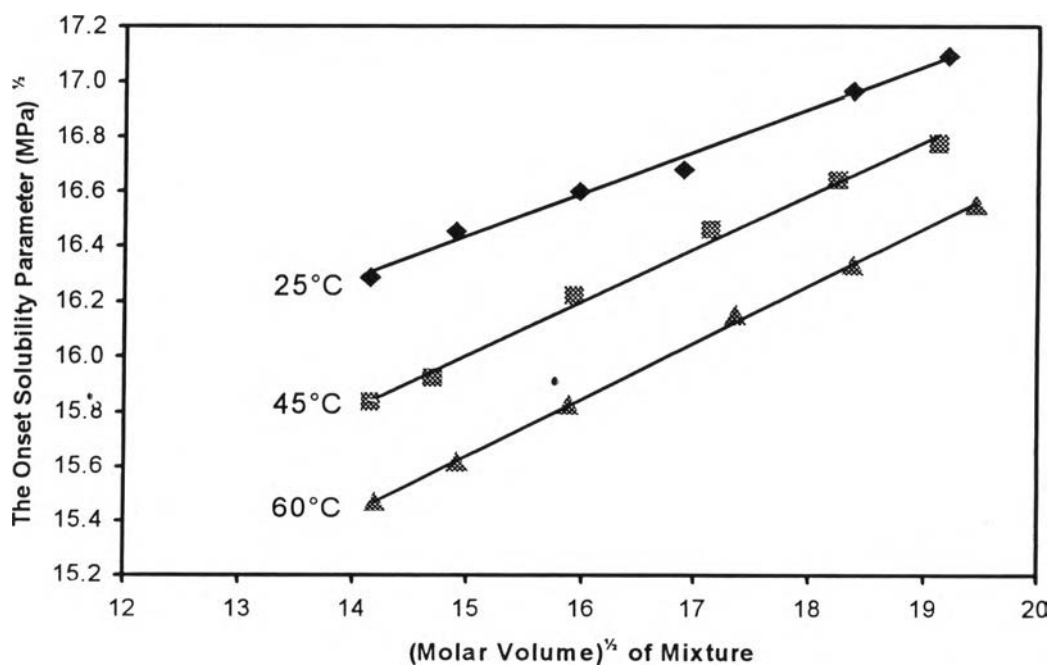


Figure 4.26 The onset solubility parameter of Oil C heavy oil titrated with different normal alkanes at different temperatures plotting with the square root of the molar volume of the mixture.

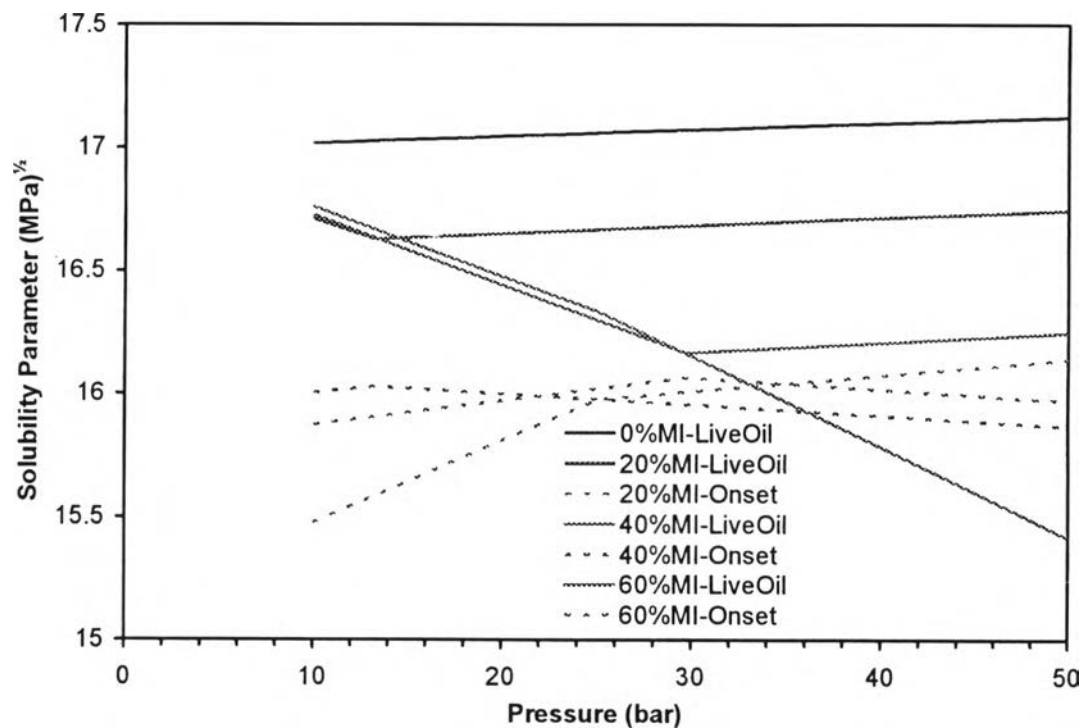


Figure 4.27 The live oil solubility parameter and the onset solubility parameter prediction of Oil C heavy oil with different ratios of n-butane added.

The Oil C field is considering using solvent injection with the steam to reduce the viscosity as stated earlier. The effect of n-butane injection is shown in Figure 4.27. At about 60 mole% n-butane, asphaltene will precipitate out of the crude oil at reservoir pressure (34 bar). Therefore, n-butane injection of less than 60 mole% is preferred to avoid asphaltene precipitation.