



CHAPTER IV RESULTS AND DISCUSSION

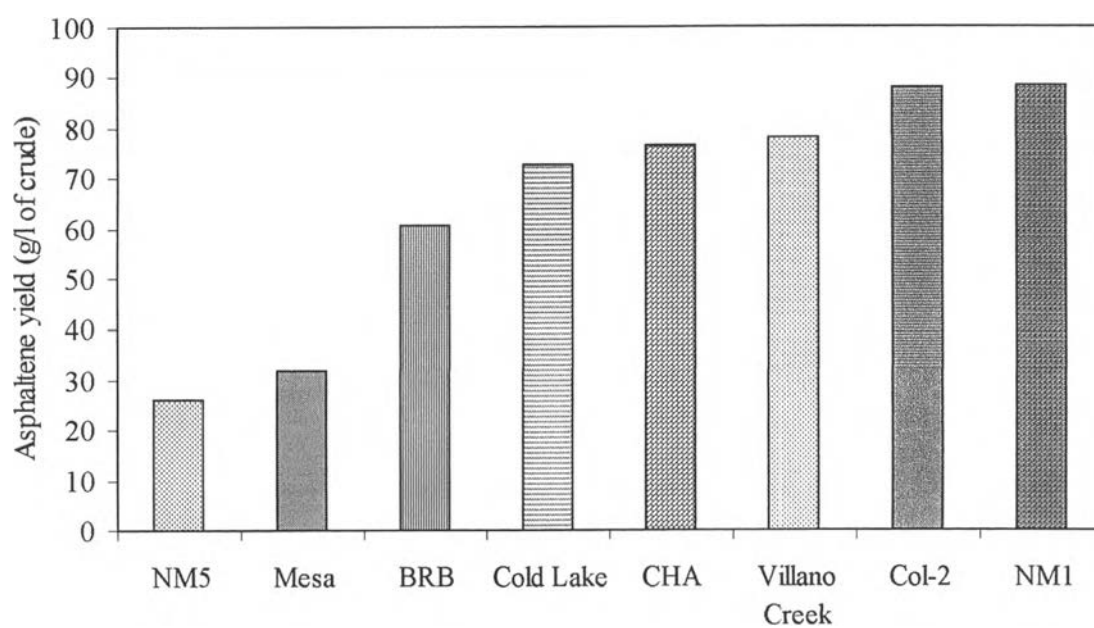
4.1 Yields and Fractionation of Asphaltenes

Table 4.1 shows the SARA analysis for the compositions of two types of crude oils, NM1 and NM5. NM1 crude contained much higher amounts of asphaltenes, approximately 4 times than those of NM5. Figure 4.1 shows the yields of asphaltenes g/l of eight crude oils. The yields obtained from NM1, NM5, Mesa, Cold Lake, Col-2, CHA, BRB, and Villano Creek crude oils were about 90, 26, 32, 73, 90, 77, 61, and 78 grams of asphaltenes per liter of crude oil, respectively.

The asphaltenes obtained from the ASTM precipitation procedure were then fractionated into subfractions having different polarities. For NM1, Mesa, Col-2, and BRB, the first fraction, F60/40, which came out by adding pentane (60% by volume) to the solution of asphaltene with methylenechloride, is the most polar fraction whereas for NM5, Cold Lake, CHA, and Villano Creek, the first fraction, F70/30, is the most polar fraction. Next the volume ratio of pentane to methylenechloride was successively increased to 70:30, 80:20, and 90:10 and the precipitates collected in each step were named F60/40, F70/30, F80/20, and F90/10, respectively (Nalwaya et al., 1999). Fractionation results of all eight asphaltenes are shown in Figure 4.2. NM1, Mesa, and Col-2 asphaltenes were mainly composed of the high polar fractions of F60/40 and F70/30. On the other hand, NM5, Cold Lake, CHA, and Villano Creek asphaltenes were found to contain no high polar fractions of F60/40. Cold Lake, CHA, BRB, and Villano Creek were mainly composed of the polar fractions of F70/30 and F80/20 whereas NM5 was mainly composed of the less polar fractions of F80/20 and F90/10.

Table 4.1 SARA analysis of two crude oils.

| Crude oil | Saturates (%) | Aromatics (%) | Resins (%) | Asphaltenes (%) |
|-----------|---------------|---------------|------------|-----------------|
| NM1 | 29.9 | 44.3 | 17.9 | 7.9 |
| NM5 | 43.5 | 43.2 | 11.3 | 2.0 |

**Figure 4.1** The asphaltene yields precipitated from eight crude oils.

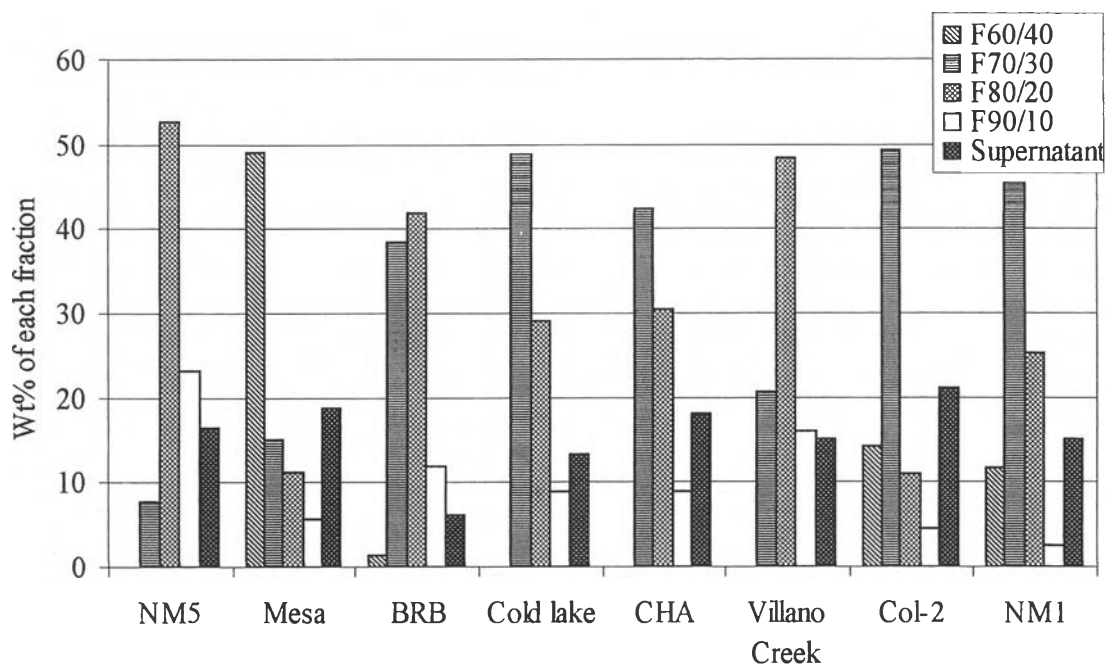


Figure 4.2 The fractionation yields of eight asphaltenes.

4.2 Solubilities of Unfractionated Asphaltenes in Toluene/Heptane

In this study, the solubility of NM1, NM5, Mesa, Cold Lake, Col-2, CHA, BRB, and Villano Creek asphaltenes in various toluene/heptane solutions were measured. The solubilities of these unfractionated asphaltenes in toluene/heptane solvent were shown in Figure 4.3. It was found that the solubility of these asphaltenes increased when increasing the percent volume of toluene in the solvent mixture. The solubility of NM5 asphaltene was the highest among those of asphaltenes studied, while the solubility of Col-2 was the lowest. The solubilities of NM1 and Mesa asphaltenes were slightly higher than that of Col-2 asphaltene whereas the solubilities of CHA, BRB, Villano Creek, and Cold Lake were quite similar and lower than that of NM5 asphaltene.

As discussed previously, Col-2, NM1, and Mesa asphaltenes were composed of approximately the same weight percentage of the higher polar fractions, F60/40 and F70/30. Consequently, their solubility properties were virtually the same and were relatively higher than those of the other asphaltenes. This result can be explained for CHA, BRB, Villano Creek, and Cold Lake asphaltenes, which were

mainly composed of essentially the same weight percentage of the polar fractions of F70/30 and F80/20. Their solubility values were also similar and were relatively higher than that of NM5 asphaltene, which was mainly composed of the less polar fractions. This result can partially be explained by the effect of the polarity of asphaltenes on solubility, except Mesa asphaltenes. The higher the polarity of asphaltenes resulted in the lower their solubility.

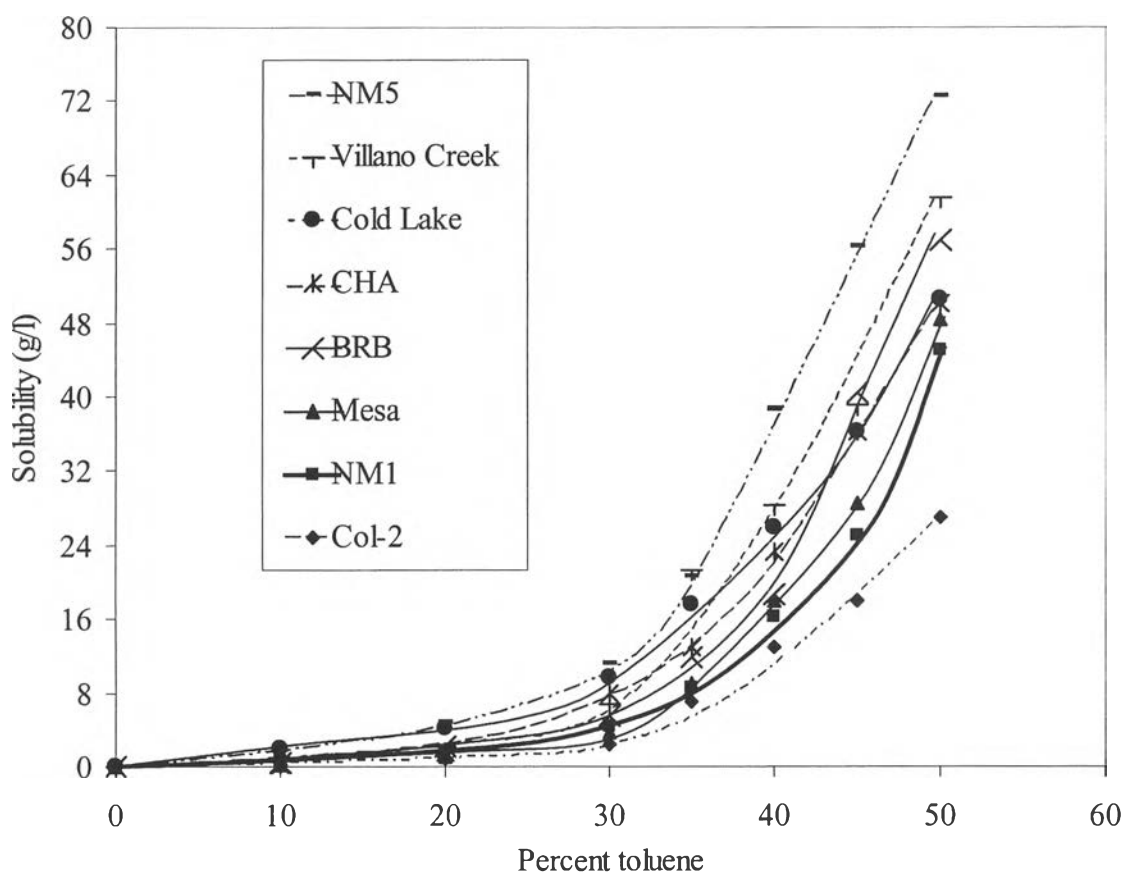


Figure 4.3 Solubilities of unfractionated asphaltenes as a function of percent toluene in heptane.

4.3 Solubility of NM1 and NM5 Asphaltenes in Different Aromatics/Heptane Solvents

Figure 4.4 shows the solubilities of NM1 and NM5 asphaltenes in the different aromatics/heptane solvents at 25°C. The solvents used in this study were toluene and 1-methyl naphthalene as aromatic and decalin as dicyclohexane

component. It was observed that both NM1 and NM5 asphaltenes could be dissolved more easily in 1-methyl naphthalene, toluene and decalin, respectively. The reason is that 1-methyl naphthalene is a 2-ring aromatic component. The structure of 1-methyl naphthalene is similar to that of asphaltene, whereas toluene is a 1-ring aromatic component and decalin is dicyclohexane component, which is not aromatic. Asphaltenes are mainly composed of a cluster of polyaromatic nuclei so that they can be better dissolved in the denser aromatic components.

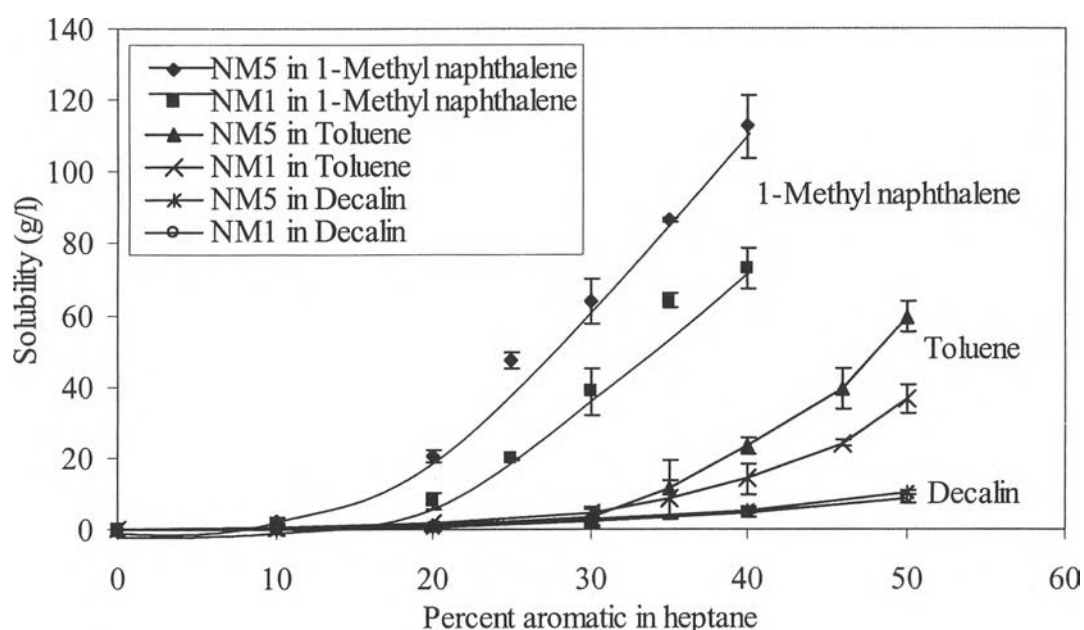


Figure 4.4 Solubility of unfractionated NM1 and NM5 asphaltenes as a function of various kinds of aromatic solvents in heptane.

4.4 Effect of Temperature on Asphaltene Solubility

Figures 4.5 and 4.6 show the solubilities of NM1 and NM5 asphaltenes at different temperatures in the toluene/heptane, 1-methyl naphthalene/heptane, and decalin/heptane solvents, respectively. The temperatures used in this study were 4, 25, and 45°C. It was found that the higher the temperature, the more easily both NM1 and NM5 asphaltenes can be dissolved.

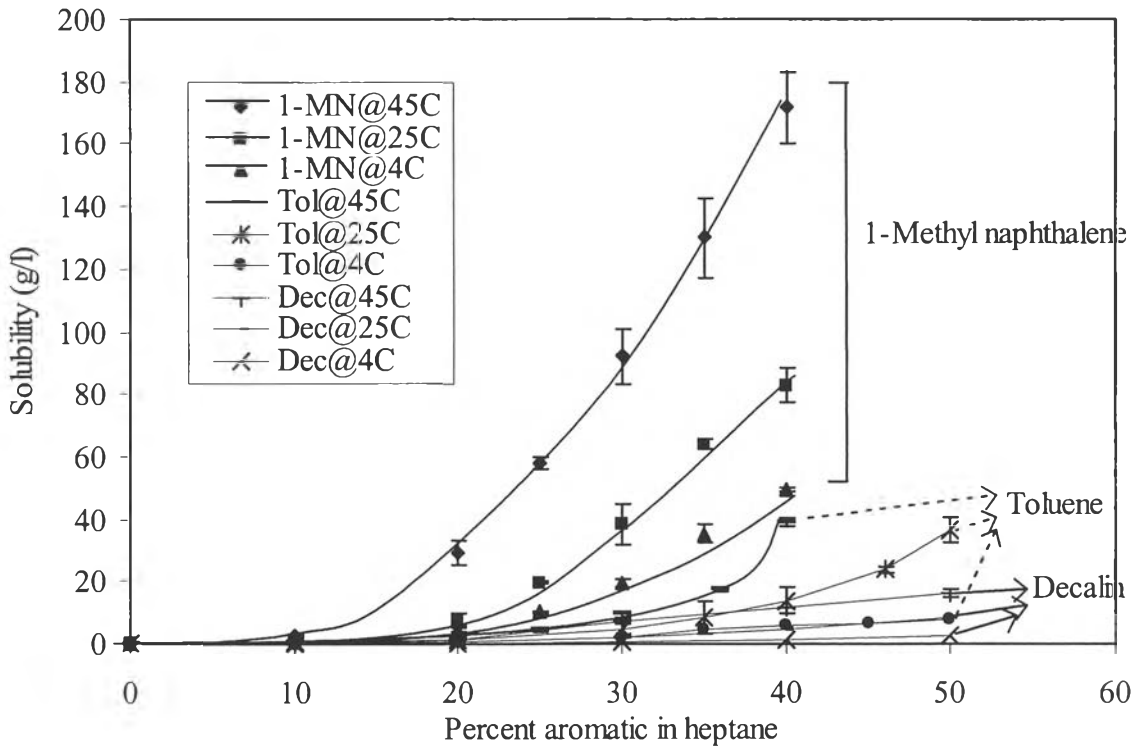


Figure 4.5 Solubility of unfractionated NM1 asphaltene as a function of temperature in aromatic/heptane solvents.

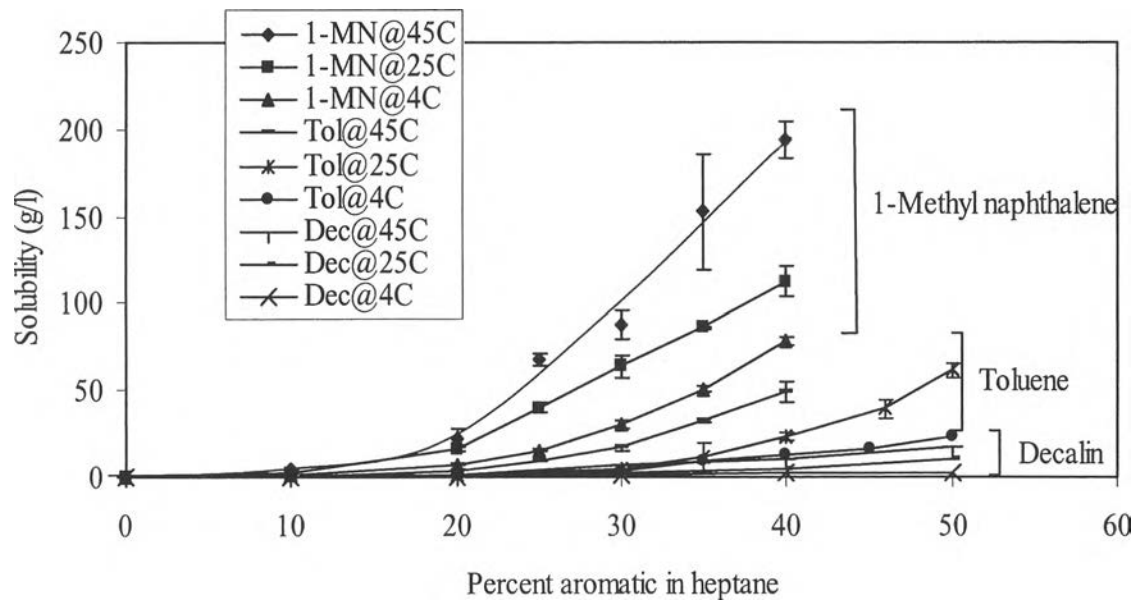


Figure 4.6 Solubility of unfractionated NM5 asphaltene as a function of temperature in aromatic/heptane solvents.

Figure 4.7 shows the effect of temperature on the solubilities of NM1 and NM5 asphaltenes in toluene/heptane. The results revealed that temperature had the significant effect on the solubility of both NM1 and NM5 asphaltenes at the higher percentages of toluene in heptane. At low percentages of toluene in heptane, an increase in temperature insignificantly affected the solubility of both asphaltenes. Even the temperature was increased; the low percentages of aromatic solvents resulted in the low polar medium for asphaltene to dissolve. On the other hand, at the high percentages of toluene in heptane, increases in temperature did affect the solubility of both asphaltenes.

Temperature has significant effect on the solubility of both asphaltenes at the higher percentages of 1-methyl naphthalene and decalin in heptane, as shown in Figures 4.8 and 4.9, respectively. In addition, the greatest effect of temperature on the solubility of asphaltenes was observed at the highest percentage of 1-methyl naphthalene in heptane, such as at a 40 vol% 1-methyl naphthalene in heptane, for both NM1 and NM5 asphaltenes as shown in Figure 4.10.

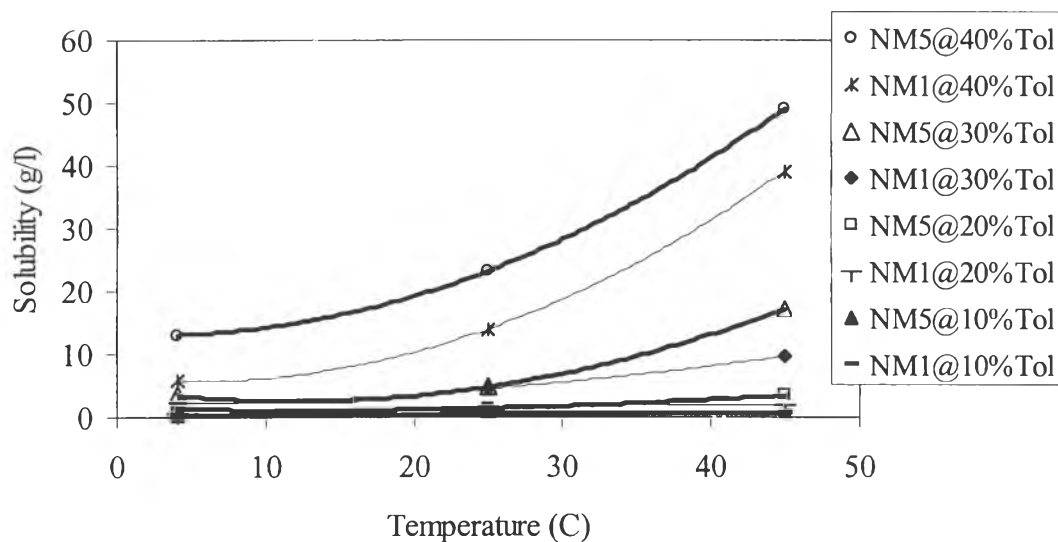


Figure 4.7 The effect of temperature on solubility of NM1 and NM5 asphaltenes for different percentages of toluene in heptane.

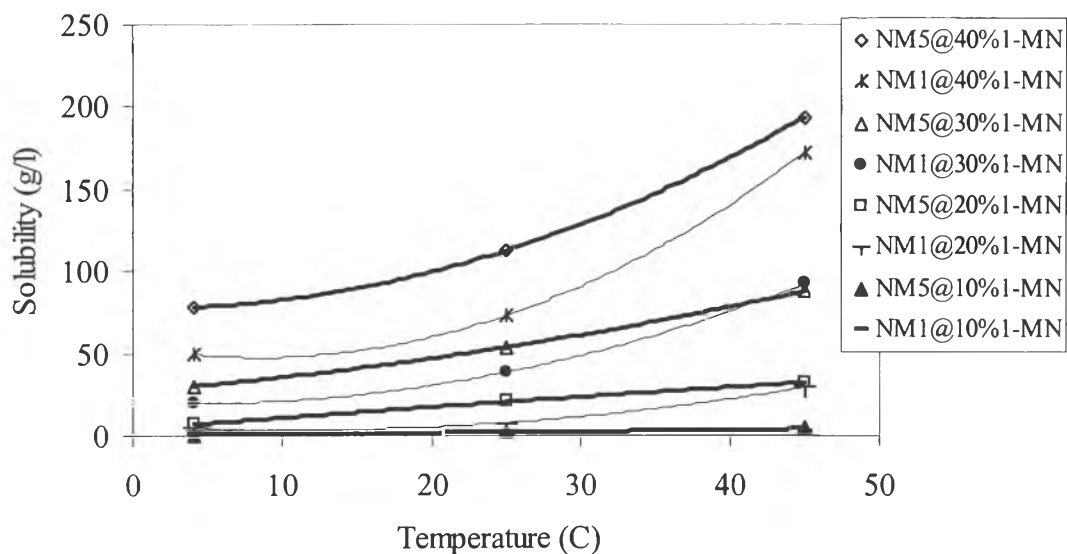


Figure 4.8 The effect of temperature on solubility of NM1 and NM5 asphaltenes for different percentages of 1-methyl naphthalene in heptane.

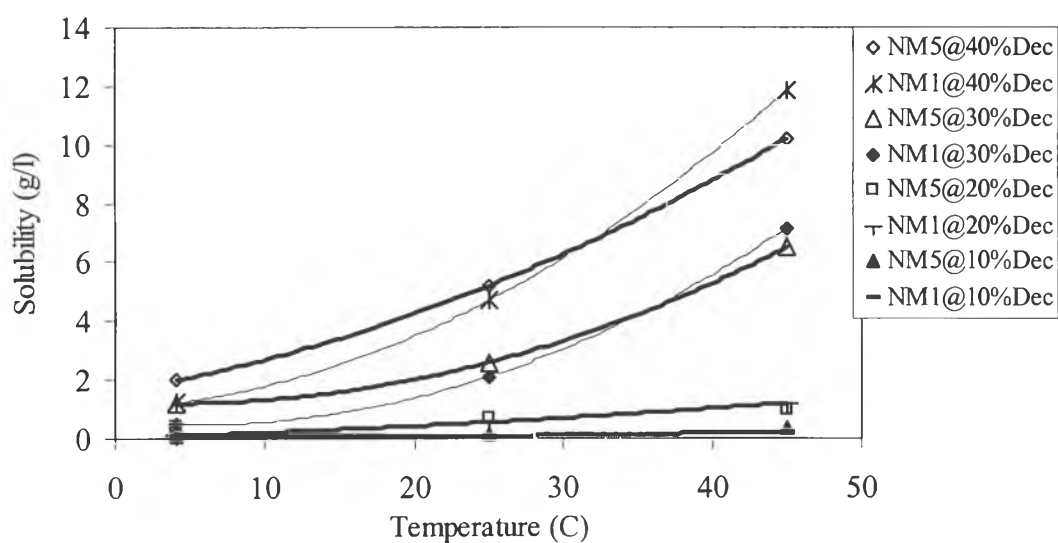


Figure 4.9 The effect of temperature on solubility of NM1 and NM5 asphaltenes for different percentages of decalin in heptane.

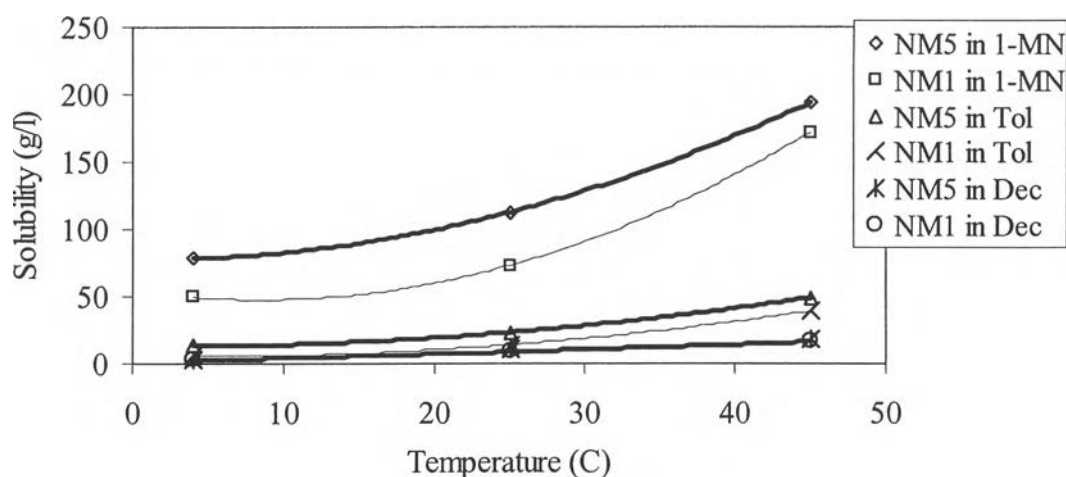


Figure 4.10 The effect of temperature on solubility of NM1 and NM5 asphaltene at 40 vol% 1-methyl naphthalene, toluene, and decalin in heptane.

4.5 Solubility of Fractionated Asphaltenes

Figure 4.11 shows the solubility of different polar fractions of NM1 (unstable) asphaltene. It was found that the asphaltene solubility increased as the polarity of asphaltene decreased. Also, the solubility of each fraction increased with an increase in the percentage of toluene in the solvent mixture. The later result was the same as that for the unfractionated asphaltene; there were critical percent volumes of toluene in the solvent mixture resulted in drastically increasing the asphaltene solubility. Forty volume percentage of toluene in the solvent mixture was required to increase the solubility of the least polar fraction, F90/10, significantly. As shown in Figure 4.11, there is no difference in the solubility of all polar fractions for the percentage of toluene lower than the critical values. On the other hand, there was a significant difference in the solubility of all polar fractions for the percentage of toluene higher than the critical values. The solubility of unfractionated NM1 asphaltene lies between the solubility of its all polar fractions.

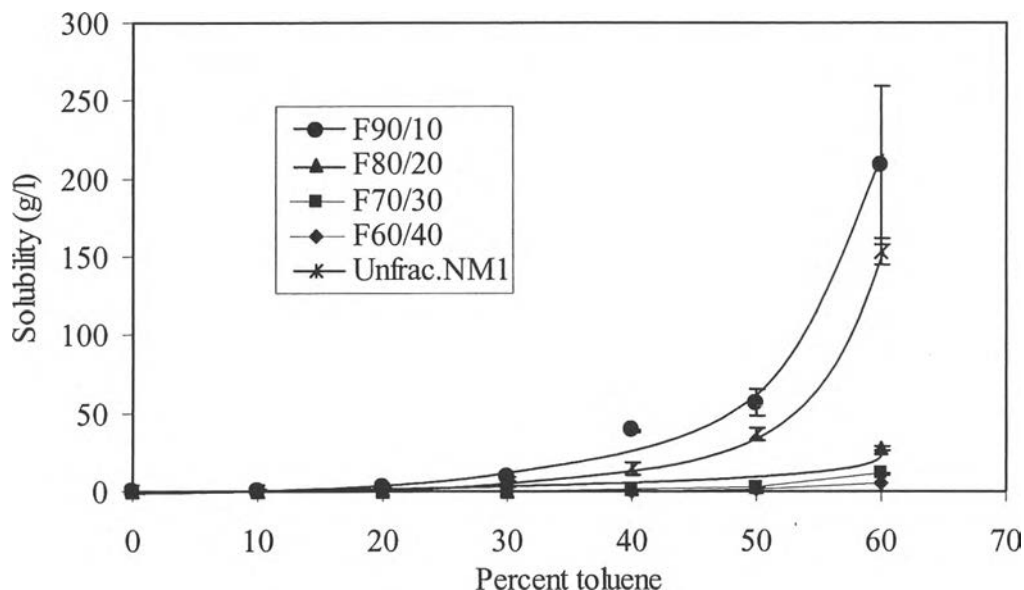


Figure 4.11 Solubility of NM1 asphaltene as a function of percent toluene of different polar fractions at 25°C.

4.6 Effect of Aging on Asphaltene Solubility

Figure 4.12 shows the solubility of unaged, nitrogen aged, oxygen aged and air aged Cold Lake asphaltenes in toluene/heptane solvent. It was observed that the unaged asphaltenes had a slightly greater solubility than those of nitrogen aged, oxygen aged, and air-aged asphaltenes, respectively. Due to nitrogen is an inert gas and oxygen is an oxidized gas, the solubility of nitrogen aged asphaltenes is slightly greater than that of oxygen and air aged asphaltenes. However, there was no significant difference in the solubility of oxygen aged and air-aged asphaltenes. It has been found that two reactions occurring during aging process are oxidation reaction and condensation polymerization reaction (Soontravanich, 1999). One explanation for the indifference of solubility of these two asphaltenes aged in air and oxygen is that the aging time was not sufficiently long enough for these reactions to occur during the aging procedure.

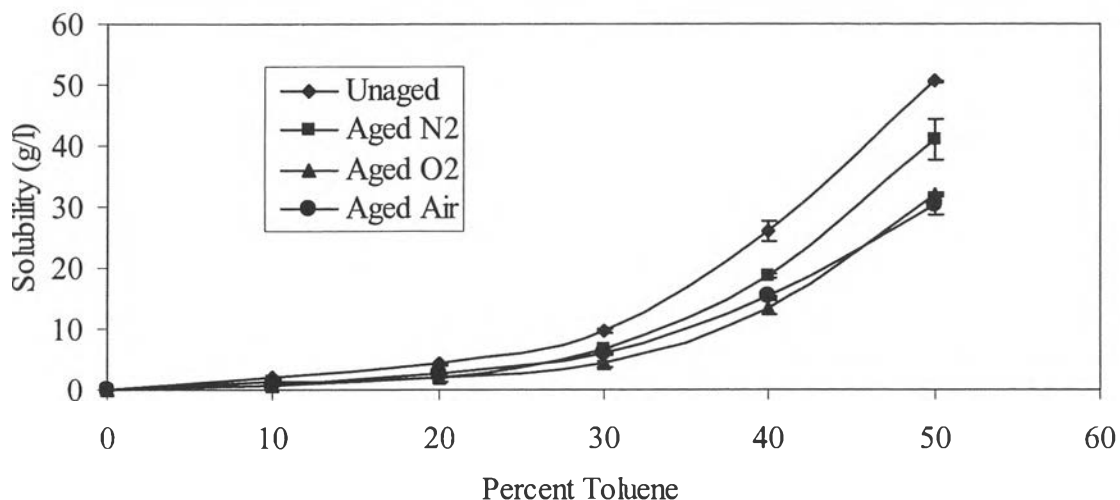


Figure 4.12 Solubility of Unaged, nitrogen aged, oxygen aged and air aged Cold Lake asphaltenes in toluene/heptane solvent.

4.7 Prediction of Molecular Weight of Asphaltene from Solubility Data

Solubility of asphaltenes can be calculated from the equilibrium ratio as defined in Equations 2.3 and 2.6 for the single component solubility parameter and for the three component solubility parameter models, respectively. The asphaltene molar volumes and solubility parameters are estimated from Equations 2.4 and 2.5, respectively, for the single component solubility parameter model and from Equations 2.4, and 2.7, respectively, for the three-component solubility parameter model. For the single component model, two cases were studied, assuming the value of 0.44 for A (Kongthawornsuk, 2001) for predicting only asphaltene molecular weight (Case1) and letting the model find the best fit of A in Equation 2.5 and asphaltene molecular weight (Case 2).

To investigate the sensitivity of the model from the three-component model, the values of 0.011 and 0.44 for ψ_1 in Equation 2.8a and A_d in Equation 2.7a were used as the initial guesses to find the best fitted asphaltene molecular weight (Case 3). However, there are 3 unknown variables which are ψ_1 , ψ_2 , in Equations 2.8a and 2.8b, respectively, and MW. That makes the three-component model is much more complicated. The different input of initial guess will give the different value of molecular weight. Manistu and *coworker* (1997) recommended that the

values of 0.011 and 4 were assumed for ψ_1 in Equation 2.8a and ψ_2 in Equation 2.8b, respectively, because these are the ratios for known compounds most similar to asphaltenes: ethylbenzene and naphthalene (Case 4). The values of 0.011, 4 and 0.44 are also assumed for ψ_1 , ψ_2 and A_d (Kongthawornsuk, 2001), respectively in Case 5. Based on the experimental solubility data, the prediction of asphaltene molecular weights can be determined from Equation 2.10 using the Solver mode in Microsoft Excel.

By assuming these values of ψ_1 and ψ_2 , the only unknown parameter is the molecular weight of the asphaltenes, MW_{asph} , because:

$$\delta_p = 0.011 \delta_d$$

$$\delta_h = 0.011 * 4 * \delta_d = 4\delta_p$$

and δ_d is related to MW_{asph} by Equation 2.7a.

For finding the MW_{asph} with the 1-component model, Equation 2.10 was used with Equation 2.3, and for the 3-component model, Equation 2.10 was used with Equation 2.6.

The calculated solubility values from 1-component and 3-component solubility parameter models along with the experimental solubility data of both unfractionated and fractionated asphaltenes in toluene/heptane at 25°C are plotted comparatively as shown in Figures 4.13, 4.14, 4.15, 4.16, 4.17 and 4.18 for unfractionated NM1, unfractionated NM5, F60/40, F70/30, F80/20 and F90/10 asphaltenes, respectively. The calculated values from both models agree very well with the experimental data. When dispersion forces dominate, i.e., for nonpolar solvent, Equation 2.6 reduces to Equation 2.3 and the predictions are expected to coincide (Mannistu *et al*, 1997).

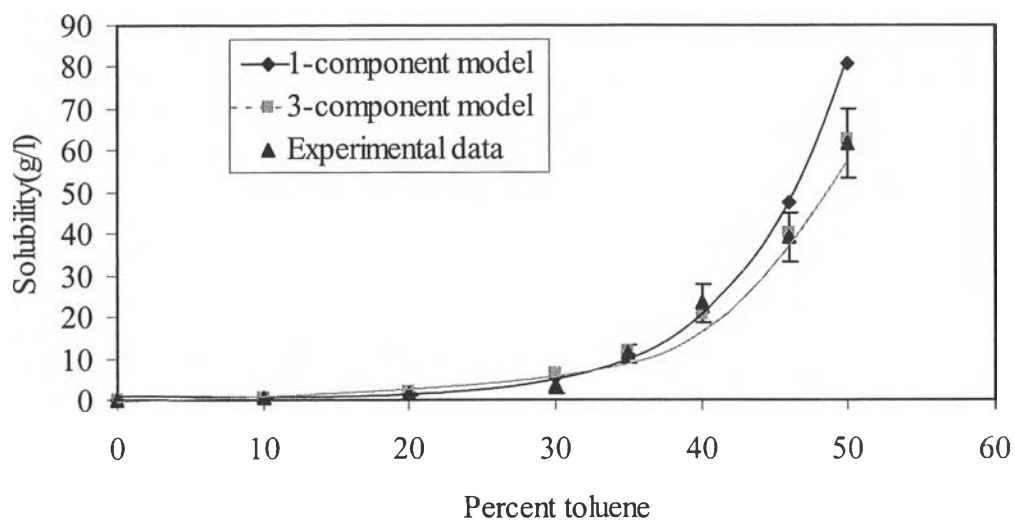


Figure 4.13 Comparison between the predicted solubility values from both 1-component and 3-component solubility parameter models for unfractionated NM1 in toluene/heptane solvent.

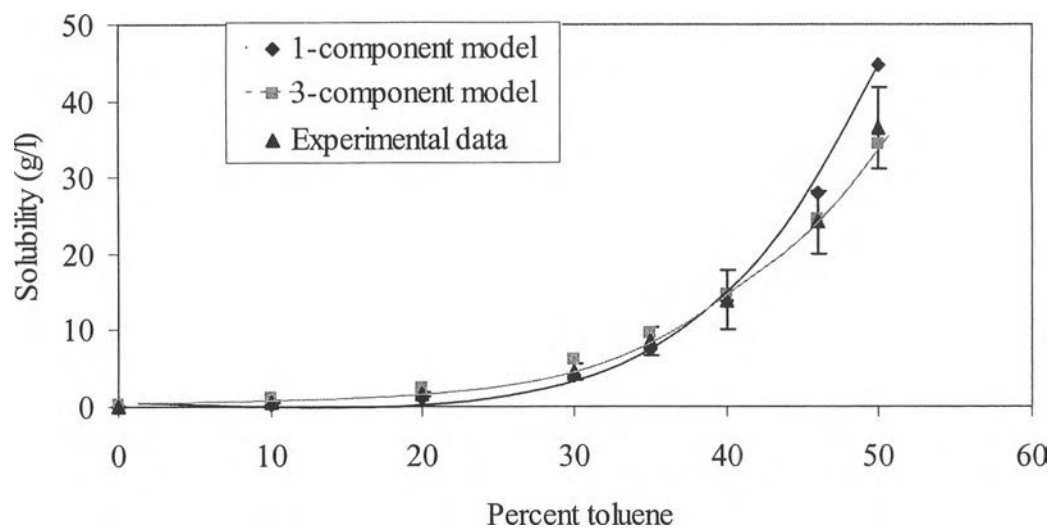


Figure 4.14 Comparison between the predicted solubility values from both 1-component and 3-component solubility parameter models for unfractionated NM5 in toluene/heptane solvent.

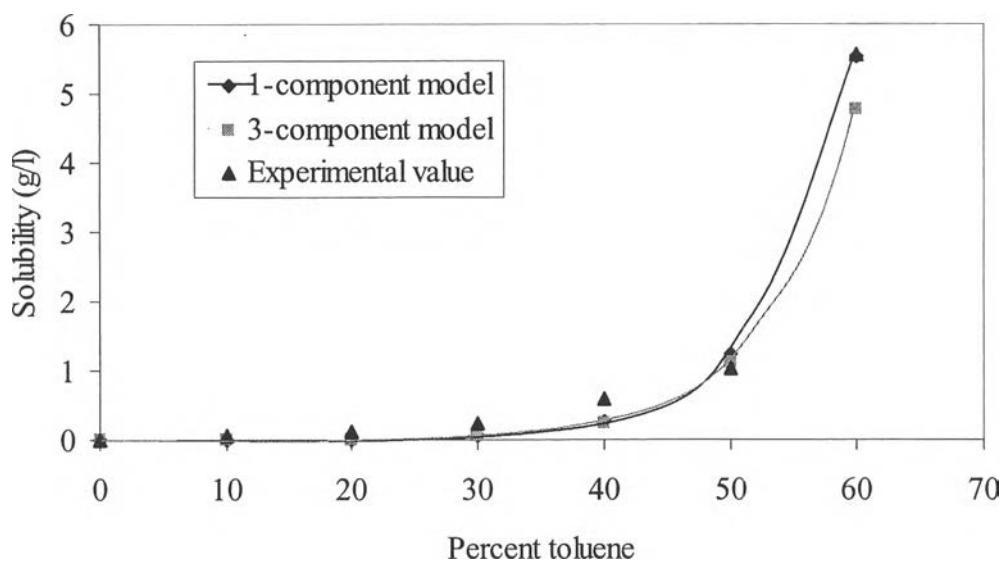


Figure 4.15 Comparison between the predicted solubility values from both 1-component and 3-component solubility parameter models for F60/40 NM1 in toluene/heptane solvent.

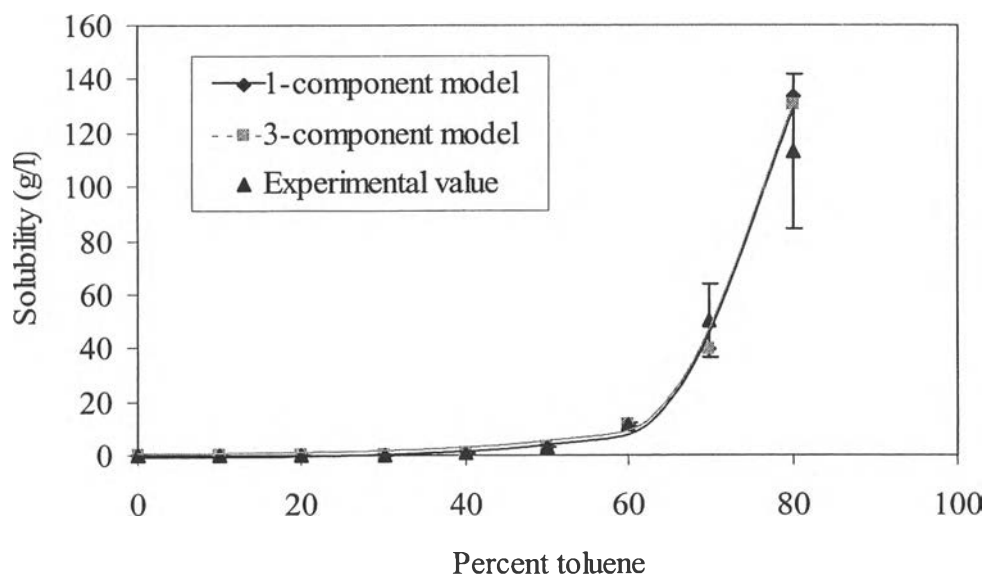


Figure 4.16 Comparison between the predicted solubility values from both 1-component and 3-component solubility parameter models for F70/30 NM1 in toluene/heptane solvent.

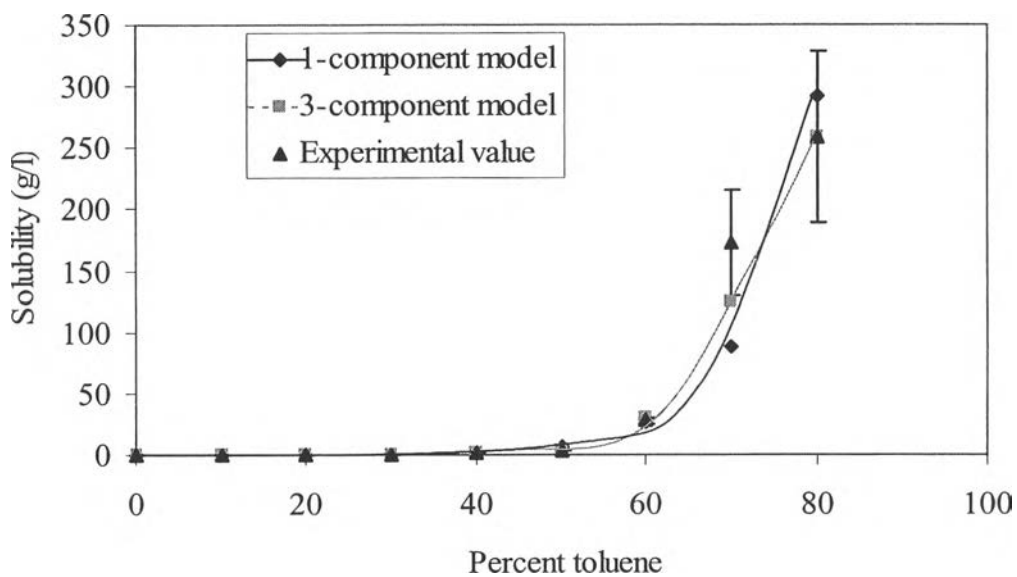


Figure 4.17 Comparison between the predicted solubility values from both 1-component and 3-component solubility parameter models for F80/20 NM1 in toluene/heptane solvent.

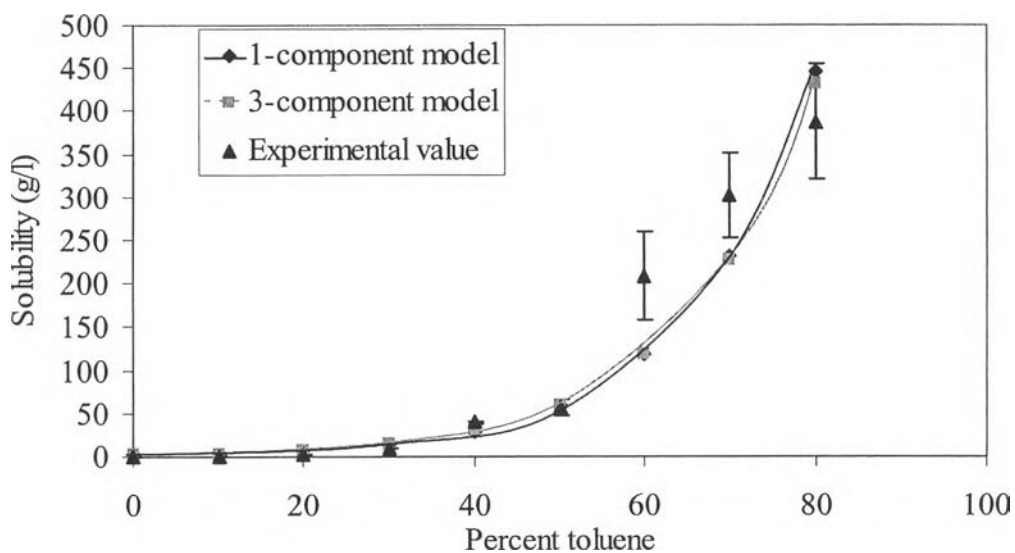


Figure 4.18 Comparison between the predicted solubility values from both 1-component and 3-component solubility parameter models for F90/10 NM1 in toluene/heptane solvent.

The predicted values of molecular weights from both 1-component and 3-component solubility parameter models of unfractionated and fractionated asphaltenes in all cases were also shown in Table 4.2. The predicted molecular weight increased as the polarity of the asphaltene fraction increased. In the case of assuming all parameters as a constant and predicting only asphaltene molecular weight for both 1-component and 3-component models, it was observed that the predicted molecular weight of NM1 asphaltene was greater than that of NM5 asphaltene. The NM1 asphaltene contained a greater amount of the high polar fraction compared to that of NM5 asphaltene; therefore, NM1 asphaltene has a higher predicted molecular weight than that of NM5. The higher molecular weight can also be interpreted as an increased ability to aggregate in dilute solution due to increased polarity (Andersen and Speight, 1999). This result could be explained by the heteroatom content of the high polar fraction, which results in the higher values of the molecular weight (Andersen, 1994). However, in the case of not assuming all parameters as a constant, the predicted molecular weight of NM5 asphaltene was greater than that of NM1 asphaltene and in some cases the predicted molecular weight of F80/20 was higher than that of F70/30. This result could be explained by the sensitivity of the models. As stated earlier, different input of initial guess will lead to different molecular weight of asphaltene.

The most important factors for predicting the molecular weight of asphaltenes were the values of A , ψ_1 , and ψ_2 in Equations 2.5, 2.8a, and 2.8b, respectively. In the case of assuming the values of 0.011 and 4, which are the ratios of known compounds most similar to asphaltenes: naphthalene, for ψ_1 and ψ_2 , respectively, would also give the uncertain predicted molecular weight of asphaltene. The reason is because asphaltenes are far more complicated compound than naphthalene. The molecular weights obtained through fitting the data to the different input ψ_1 and ψ_2 are very different and may, as such, be hypothetical without any physical meaning. These molecular weights represent, in theory, the property of the dissolved molecules (Andersen and Speight, 1999).

Table 4.2 The predicted molecular weight of asphaltenes.

| Asphaltenes | 1-component model | | | 3-component model | | | | |
|-------------|-------------------|--------|-------|-------------------|-------|--------|-------|--------|
| | Case 1 | Case 2 | | Case 3 | | Case 4 | | Case 5 |
| | MW | MW | A | MW | Ad | MW | Ad | MW |
| Unfrac. NM5 | 757 | 1021 | 0.43 | 872 | 0.43 | 813 | 0.42 | 481 |
| Unfrac. NM1 | 852 | 670 | 0.45 | 832 | 0.438 | 673 | 0.43 | 572 |
| F60/40 NM1 | 3065 | 1119 | 0.468 | 1114 | 0.46 | 1038 | 0.45 | 1246 |
| F70/30 NM1 | 2522 | 924 | 0.47 | 996 | 0.456 | 862 | 0.451 | 1053 |
| F80/20 NM1 | 1779 | 1428 | 0.445 | 690 | 0.289 | 1541 | 0.422 | 1037 |
| F90/10 NM1 | 820 | 885 | 0.438 | 542 | 0.446 | 472 | 0.438 | 457 |

Case 1: Fixed the value of $A = 0.44$, let the model find the best fit of MW only.

Case 2: Let the model find the best fit of both A and MW .

Case 3: Fixed $\psi_2 = 4.0$, input $\psi_1 = 0.011$ and $A_d = 0.44$ as initial guess and let the model find the best fit of MW .

Case 4: Fixed $\psi_1 = 0.011$ and $\psi_2 = 4.0$, let the model find the best fit of MW .

Case 5: Fixed $\psi_1 = 0.011$, $\psi_2 = 4.0$ and $A_d = 0.44$, let the model find the best fit of MW .

Molecular weights of for the NM1 and NM5 asphaltenes used in the solubility experiments have been reported to be 2100 g/mol and 3090 g/mol, respectively, using vapor pressure osmometry of solutions in methylenechloride. These data were provided by PDVSA-Intevep Company, Venezuela. There is a significant difference in the magnitude of the molecular weights as calculated herein and those reported from the experimental measurements. The asphaltenes were assumed to be uniform in chemical features in the above calculations. However, the asphaltenes are known to be a variation of molecular types of varying polarity and molecular weight (Andersen and Speight, 1999).

The predicted values of molecular weights from both 1-component and 3-component solubility parameter models of different ranges of toluene percentages by fixing $A = 0.44$ for 1-component model and $\psi_1 = 0.011$ and $\psi_2 = 4.0$ for 3-component model are also shown in Table 4.3.

Table 4.3 The predicted molecular weight of asphaltenes in different ranges of toluene percentages.

| % Toluene Asphaltenes | Predicted Molecular Weight | | | | | |
|------------------------------|----------------------------|-------|-------|-------------------|-------|-------|
| | 1-component model | | | 3-component model | | |
| | 0-30 | 30-40 | 40-50 | 0-30 | 30-40 | 40-50 |
| Unfrac. NM5 | 861 | 756 | 756 | 588 | 1248 | 769 |
| Unfrac. NM1 | 831 | 842 | 852 | 671 | 738 | 793 |
| F60/40 NM1 | 909 | 964 | 1091 | 949 | 950 | 1092 |
| F70/30 NM1 | 873 | 909 | 933 | 948 | 919 | 940 |
| F80/20 NM1 | 732 | 757 | 852 | 744 | 791 | 796 |
| F90/10 NM1 | 541 | 471 | 485 | 472 | 464 | 449 |

The different ranges of data will also give the different predicted molecular weights. The properties of asphaltene should be further investigated to obtain for developing the more suitable model to predict asphaltene molecular weight. The uncertainty in molecular weight data for asphaltene precipitation and formation still needs further investigation to reveal the mechanisms, interactions, and Equilibria involved (Andersen and Speight, 1999). In models which employ the solubility parameter concept, the solubility parameter also has to be tuned to obtain a match between experiment and model, but this leads to a change in the magnitude of the tuned molecular weight. Hence, it is recommendable to keep the asphaltene solubility parameter at a fixed value and tune the molecular weight (Andersen and Speight, 1999).

The solubility parameter of asphaltenes may be obtained from spot-tests, evaluation of solubility in a range of solvent, or by flocculation titration threshold measurements (Andersen and Speight, 1999; Redelius, 2000).

In order to establish a model capable of estimating asphaltene precipitation and solubility under different conditions the present work has indicated the need of a better understanding of asphaltene chemistry (Andersen and Speight, 1999).