

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Density of Unfractionated Cold Lake Asphaltene

The density of unfractionated Cold Lake asphaltene was determined in toluene solutions. The dissolution of asphaltene in toluene was assumed to behave as a regular solution which the volume change of mixing is negligible. Therefore, the density of asphaltene in toluene solutions varied linearly with the concentration of asphaltene in solutions (%wt) as shown in Figure 4.1. Equation (4.1) expresses the relationship between density of asphaltene in a toluene solution and asphaltene concentration (Yarranton et al., 1996).

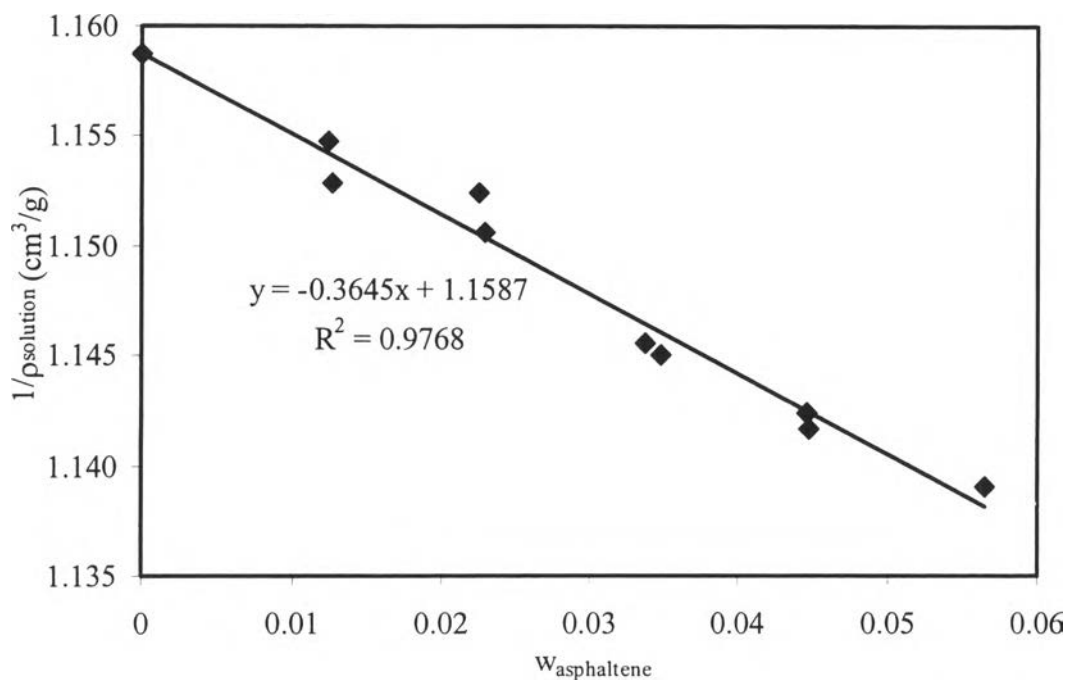


Figure 4.1 Density measurement of Cold Lake asphaltene in toluene solution.

$$\frac{1}{\rho_{\text{σολυτιον}}} = \frac{1}{\rho_{\text{σολωεντ}}} + \left(\frac{1}{\rho_{\text{ασπηαλτενε}}} - \frac{1}{\rho_{\text{σολωεντ}}} \right) \omega_{\text{ασπηαλτενε}} \quad (4.1)$$

Where ρ_{solution} = the density of asphaltene in toluene solution

ρ_{solvent} = the density of toluene

$\rho_{\text{asphaltene}}$ = the density of asphaltene

$w_{\text{asphaltene}}$ = the weight fraction of asphaltene in solution

So, the density of asphaltene is:

$$\rho_{\text{asphaltene}} = \frac{1}{\text{Slope} + \text{Intercept}} \quad (4.2)$$

Using the Equation (4.2), the density of unfractionated Cold Lake asphaltene, was obtained from the slope and intercept in Figure 4.1 was 1259.1 kg/m³. This value obtained from the present study is close to the values obtained from the ASTM D-70, 1180 kg/m³ (Peramanu *et al.*, 1999), and from pycnometer measurement, 1200 kg/m³ (Schabron and Speight, 1998 and De Hemptinne *et al.*, 1999).

4.2 Elemental and Metal Contents of Unfractionated Cold Lake Asphaltene and its Fractionation

Asphaltenes as a solubility class and have many possible structures. The elemental analysis data and molecular weight are essential information for constructing the possible asphaltene structures because elemental analysis can quantitatively tells the elemental contents in asphaltenes. Furthermore, the solubility of asphaltene can be also roughly predictable. The elemental analysis results of unfractionated Cold Lake asphaltene and its fractionated components are shown in Table 4.1.

Table 4.1 Elemental Analysis of Cold Lake asphaltene and its fractionated components

Asphaltene	Percent Weight				
	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
Unfractionated Cold Lake	81.50	7.74	1.30	2.56	8.25
F40/60 Cold Lake	80.84	7.33	1.38	2.74	7.71
F30/70 Cold Lake	81.02	7.34	1.41	2.48	7.75
F20/80 Cold Lake	81.21	7.58	1.24	1.75	8.22
F10/90 Cold Lake	80.67	7.60	1.42	2.10	8.21

The solubility of asphaltenes decreases with increasing aromatics, heteroatoms and metal contents of asphaltene molecules (Speight, 1991 and Kamiski *et al.*, 2000). The compositions of asphaltene by percent weight, shown in Table 4.1, are transformed in terms of percent mole as shown in Table 4.2. The carbon per hydrogen ratio shown in Table 4.2 indicates the most polar fraction, F40/60; of Cold Lake asphaltene has the highest aromatic-like structure while F10/90 Fraction of Cold Lake asphaltene has the highest aliphatic-like structure. Also, the percentage of heteroatoms and metal contents increases with an increasing polarity as indicated in Tables 4.2 and 4.3 (Speight, 1991 and Kamiski *et al.*, 2000). The unfractionated Cold Lake asphaltene properties are in between the properties of fractionated asphaltene. Therefore, from these results, the F10/90 Fraction of Cold Lake asphaltene should be the most soluble fraction followed by F20/80, F30/70, F40/60, respectively as we will see in next section.

Table 4.2 Carbon per hydrogen ratio and heteroatoms of Cold Lake asphaltene and its fractionated components

Asphaltene	C/H	Percent Mole	
		C+H	Heteroatom (S,O,N)
Unfractionated Cold Lake	0.8770	96.48	3.46
F40/60 Cold Lake	0.9191	96.50	3.50
F30/70 Cold Lake	0.9198	96.59	3.41
F20/80 Cold Lake	0.8930	96.93	3.07
F10/90 Cold Lake	0.8846	96.70	3.30

Table 4.3 Metal Contents of Cold Lake asphaltene and its fractionated components

Asphaltene	Al	Cr**	Cu**	Fe	Ni	V	Zn**
	%wt	Ppm	ppm	%wt	ppm	ppm	ppm
Unfractionated Cold Lake	0.10	<50	<50	0.05	56	245	<50
F40/60 Cold Lake*	0.11	<50	<50	0.01	<50**	<50**	<50
F30/70 Cold Lake	0.15	<50	<50	0.05	617	3350	<50
F20/80 Cold Lake	0.23	<50	<50	0.08	197	1010	<50
F10/90 Cold Lake	0.04	<50	<50	<0.01**	192	1240	<50

* No enough sample to repeat

** Below minimum measurable limit of instrument

4.3 Solubilities of Unfractionated Asphaltenes in Toluene/Heptane Solvent Mixtures

The solubility of unfractionated asphaltene in toluene/heptane solvent mixtures was determined by two different techniques. In the first technique, the precipitation method, asphaltene was precipitated out as heptane was added to saturated asphaltene/toluene solution. In the second technique, the solubility method, the toluene/heptane solvent mixture was added to asphaltene powder, to obtain the saturated solubility. Moreover, the effect of agitation on asphaltene solubility was also investigated. For the non-agitated system, the samples were left on the bench,

while in the agitated system the samples were shaken by a shaker continuously. The results of asphaltene solubility in various times from both systems indicated that the time it took to reach solubility equilibrium was more than five days as shown in Figure 4.2.

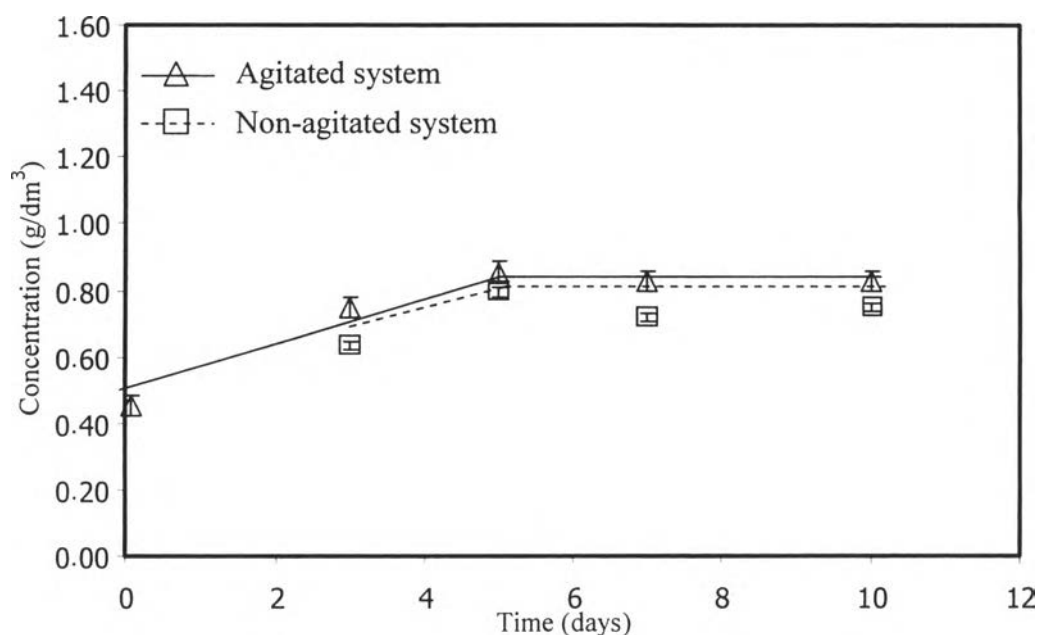


Figure 4.2 Asphaltene solubility of 30% toluene in heptane in toluene/heptane mixture as a function of time for with and without agitation using the solubility method.

In addition, the effect of agitation on asphaltene solubility is shown in Figure 4.3. The results revealed that solubilities of the non-agitated system were similar to these of the agitated system because asphaltene solubilities reached virtually the same equilibrium value.

The solubilities obtained by the different solubility techniques are shown in Figure 4.4. As can be seen in this figure, the solubilities obtained from the solubility method were higher than those from the precipitation method. This result indicates a significant interaction between the different polar fractions of asphaltene. It also leads to the fact that asphaltenes are not pure compounds, but contain several fractions which can interact with one another.

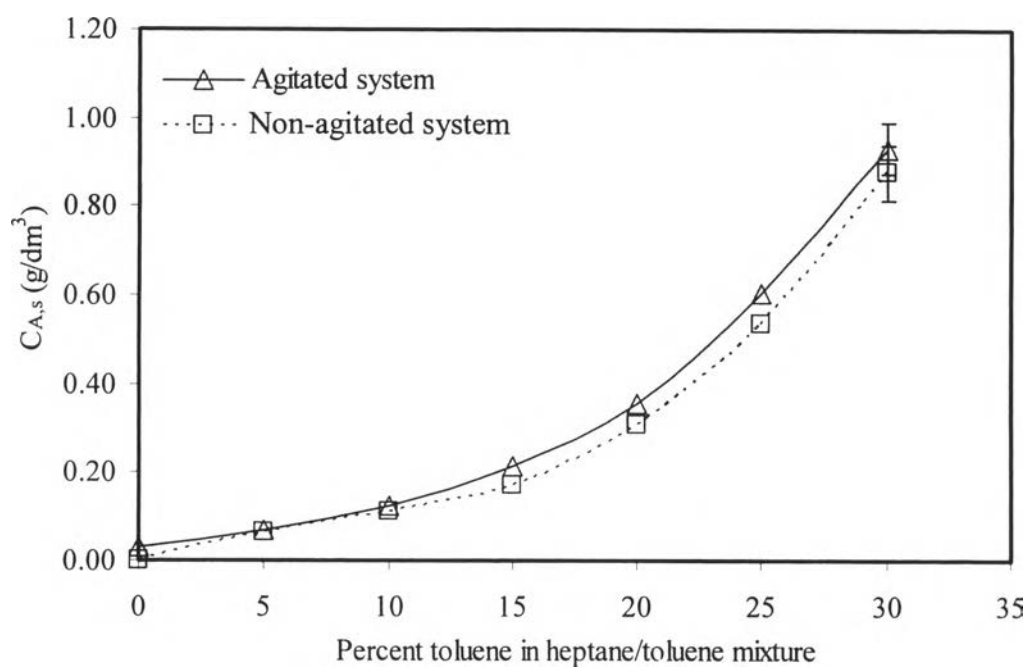


Figure 4.3 Solubilities of unfractionated Cold Lake asphaltene in non-agitated and agitated systems using solubility method.

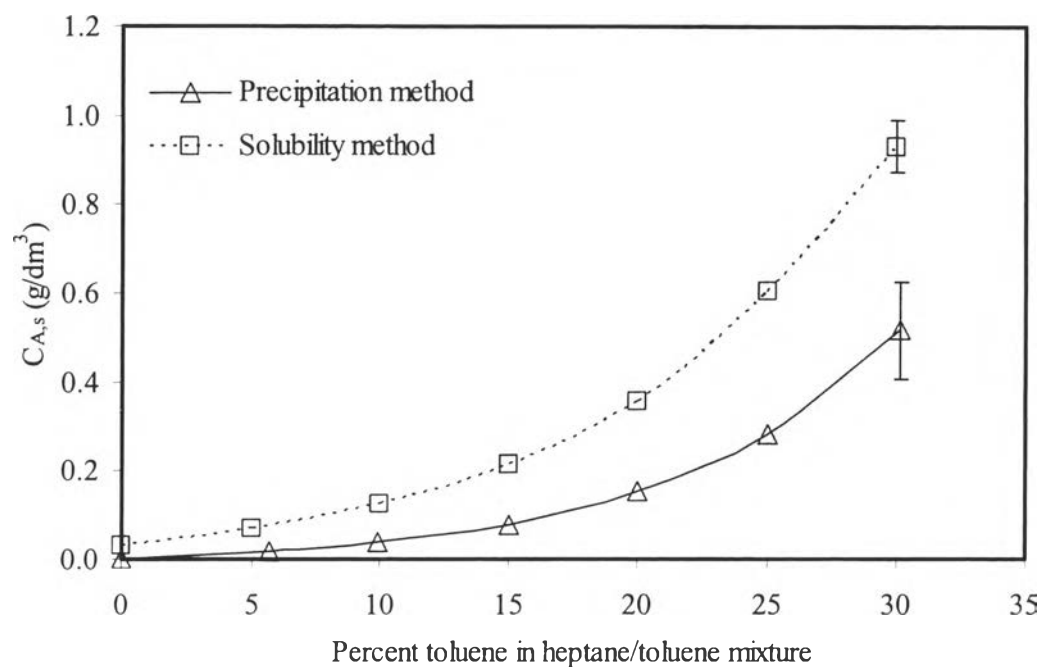


Figure 4.4 Solubilities of unfractionated Cold Lake asphaltene using different techniques with agitation system.

4.4 Solubilities of Fractionated Asphaltenes in Toluene/Heptane Solvent Mixtures

Because asphaltenes consist of several of heaviest molecules in crude oil, they cannot be characterized as a pure compound. Fractionation is an effective method used to classify the asphaltenes into small separated entities by using its polarity properties as a criterion (Nalwaya *et al.*, 1999). The solubility of fractionated Cold Lake asphaltenes was studied by using the solubility method, with agitation and the results are shown in Figure 4.5.

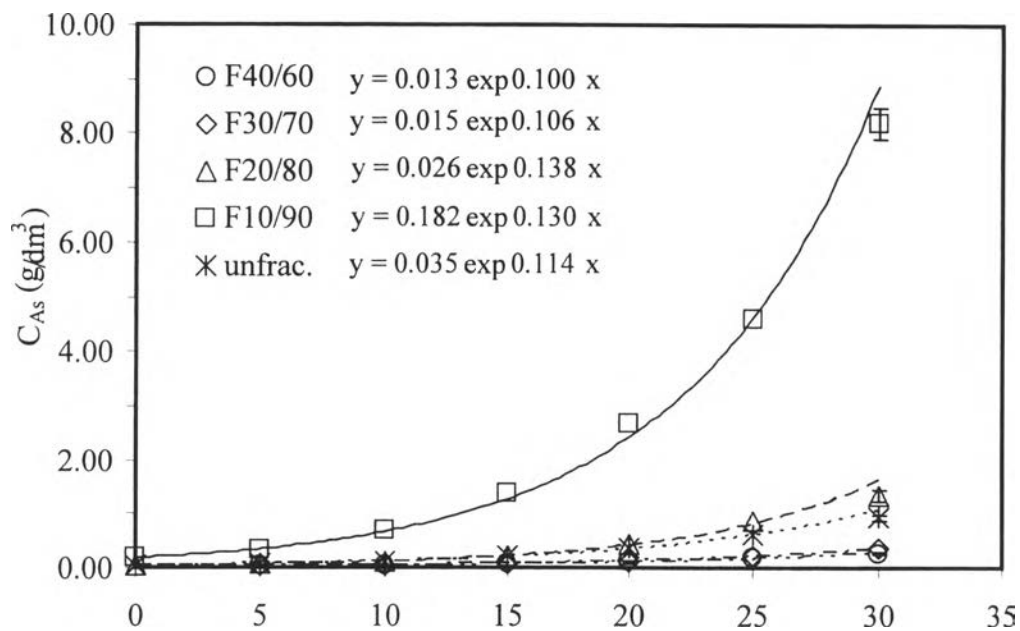


Figure 4.5 Solubility of fractionated Cold Lake asphaltene as a function of percent of toluene in heptane/toluene mixture.

As one readily observes, the solubilities are higher for the lower polar fractions. At 30% toluene in the toluene/heptane mixture, the solubilities for the fractions are 8.1923, 1.3507, 0.3580, and 0.2610 g/dm³, corresponding to the order of increased asphaltene fraction polarity. This result is in a good agreement with the dissolution experiment from the previous work (Nalwaya *et al.*, 1999). The unfractionated Cold Lake asphaltene solubility was between the solubilities of

fractionated asphaltenes because it consisted of both the high polar and low polar fractions, which were consistent with the results of elemental analysis and previous study (Poonsateansup, 2000). It is suggested that the asphaltenes' highest polar fraction became more difficult to dissolve.

4.5 Solubility Parameter Prediction of Cold Lake Asphaltene

4.5.1 Single Component Solubility Parameter Model

In this section, the molecular weights of Cold Lake asphaltene with and without fractionation are estimated using one and three component solubility parameter models. It was accomplished by using the solubility data and measured properties. The solubilities of asphaltenes can be calculated from the equilibrium ratios defined in Equation (2.5). The equilibrium ratio (K) is a function of molar volume (ν), density (ρ) and solubility parameter of asphaltenes (δ_i). The asphaltene density was obtained from the plot of asphaltene/toluene solution specific volume and asphaltene weight fraction (Figure 4.1), and the molar volume was determined from the ratio of molecular weight and density. For the one-component solubility parameter model, the ratio product of the heat of vaporization (ΔY^{vap}), kJ/mol, and molar mass i.e. the heat of vaporization per molar mass (A) were needed. The heat of vaporization and molecular weights of some aromatic hydrocarbon are shown in Table 4.4 and plotted in Figure 4.6. The heat of vaporization per molar mass (A) is the slope of Figure 4.6. Then, the asphaltene solubility parameters for the single component solubility parameter model can be determined by the product of the density obtained from Figure 4.1 and heat of vaporization per molar mass obtained from Figure 4.6. Based on the experimental solubility data and Equation (2.10), the prediction of asphaltene molecular weight can be determined by using a non-linear equation solving program written on Maple 8.

Table 4.4 Heat of vaporization and molecular weight of aromatic hydrocarbons series. (Yarranton *et al.*, 1996)

Compounds	Chemical formula	MW	Heat of vaporization (kJ/mol)
Benzene	C ₆ H ₆	78	34.39
Toluene	C ₇ H ₈	92	39.08
Naphthalene	C ₁₀ H ₈	128	56.02
1-Methylnaphthalene	C ₁₁ H ₁₀	142	60.73
Anthracene	C ₁₄ H ₁₀	178	77.65
Phenanthrene	C ₁₄ H ₁₀	178	77.65
Pyrene	C ₁₆ H ₁₀	202	88.99
Chrysene	C ₁₈ H ₁₂	228	99.28
Cold Lake (Str1)*	C ₈₀ H ₉₁ NO ₂ S ₃	1195	492.00
Cold Lake (Str2)*	C ₈₀ H ₉₁ NO ₂ S ₃	1195	459.87
Cold Lake (Str3)*	C ₇₉ H ₈₉ NO ₂ S ₃	1181	486.34
Cold Lake (Str4)*	C ₅₂ H ₅₉ NOS ₂	778	326.30
Cold Lake (Str5)*	C ₇₇ H ₈₇ NO ₂ S ₃	1155	469.00
Cold Lake (Str6)*	C ₇₇ H ₈₇ NO ₂ S ₃	1155	477.87

*The structures are drawn based on the elemental analysis data. The heats of vaporization of these molecules are determined by using group contribution theory (Barton, 1983 and 2000).

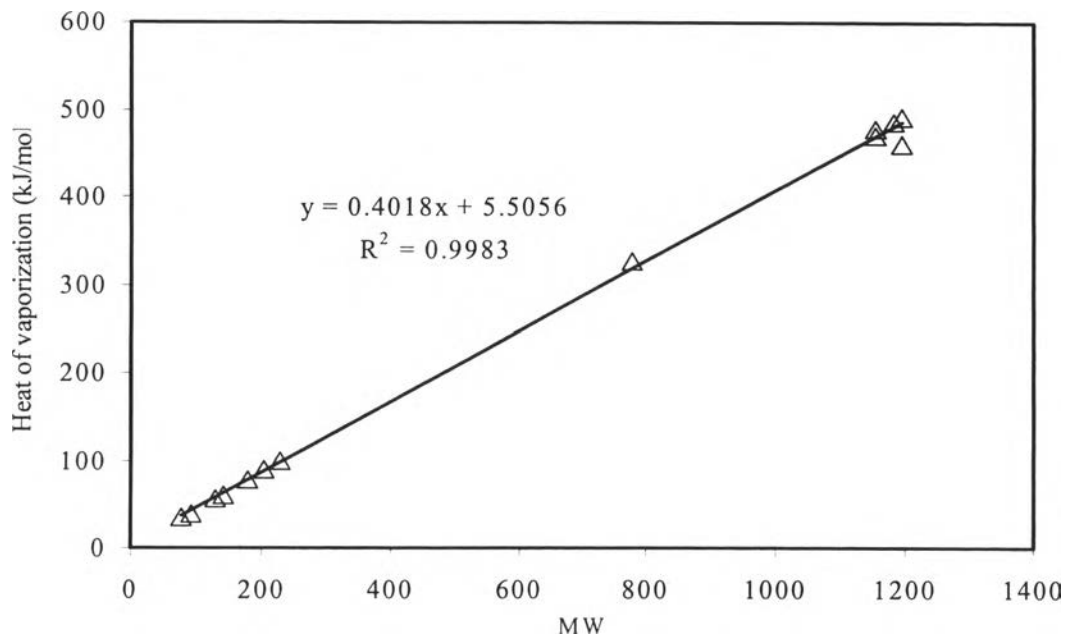


Figure 4.6 Relationship between heat of vaporization and molecular weight for aromatic hydrocarbons series.

4.5.2 Three-Component Solubility Parameter Model

Using the Hansen theory, the solubility parameters of Cold Lake asphaltene are defined by the center of its solubility space, which is an assumed pseudo-sphere shape (spheroid). To find the center coordinates δ_δ , δ_π and δ_η , the surface of solubility spheroid must be known. Since the points on the solubility curves represent the maximum amount of asphaltene dissolved in solvent mixtures. On the other hand, they are the points where asphaltenes begin to separate from the solution, the incipient precipitation points. In this calculation, the solubilities less than 0.25 g/dm^3 are considered to be insoluble. The solubility parameters at the surface of this Cold Lake asphaltene solubility spheroid can be calculated from the solvent volume fractions at precipitation points which are obtained from solubility curves of asphaltene in different binary mixtures at a particular cutoff point ($C_{A,s} < 0.25 \text{ g/dm}^3$). The binary solvent mixtures used to determine the surface of solubility spheroid in this work are toluene/heptane, toluene/acetone, toluene/methanol, toluene/allyl alcohol, nitrobenzene/heptane and nitrobenzene/acetone. Table 4.5

shows the solubility parameters of different solvents and precipitants, which were used to perform the solubility curves. The solubility of unfractionated Cold Lake asphaltene in these solvent mixture are shown in Figures 4.7 and 4.8. To give the general idea about the position of center coordinate of the solubility spheroid, asphaltene solubilities were investigated in a variety of pure solvents (see Appendix D). The same experiments were carried on with the fractionated Cold Lake asphaltene. The volumes of solvent at onset point (V_T) are shown in Table 4.6.

Table 4.5 Solubility parameters of solvents and precipitants (Barton, 2000)

Solvents	Solubility parameter (MPa ^{0.5})			
	δ_d	δ_p	δ_h	δ_t
Heptane	15.3	0	0	15.3
Acetone	15.5	10.4	7.0	20.0
Methanol	15.1	12.3	22.3	29.6
Allyl Alcohol	16.2	10.8	16.8	25.72
Toluene	18.0	1.4	2.0	18.2
Nitrobenzene	20	8.6	4.1	22.15
1-Methylnaphalene	20.7	0.8	4.7	21.2

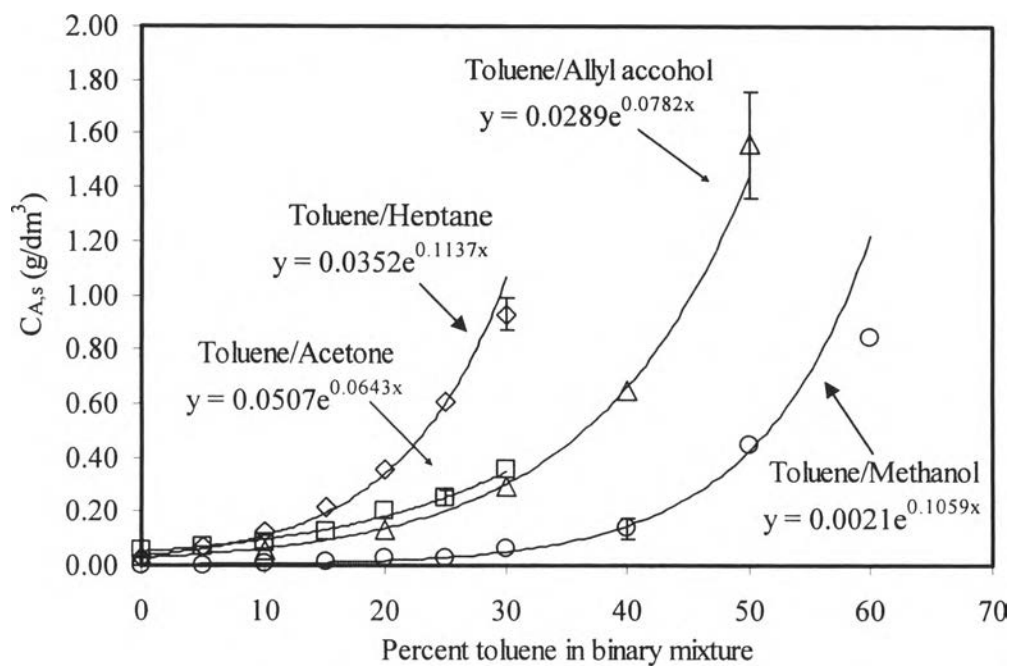


Figure 4.7 Solubility of unfractionated Cold Lake asphaltene in different toluene solutions.

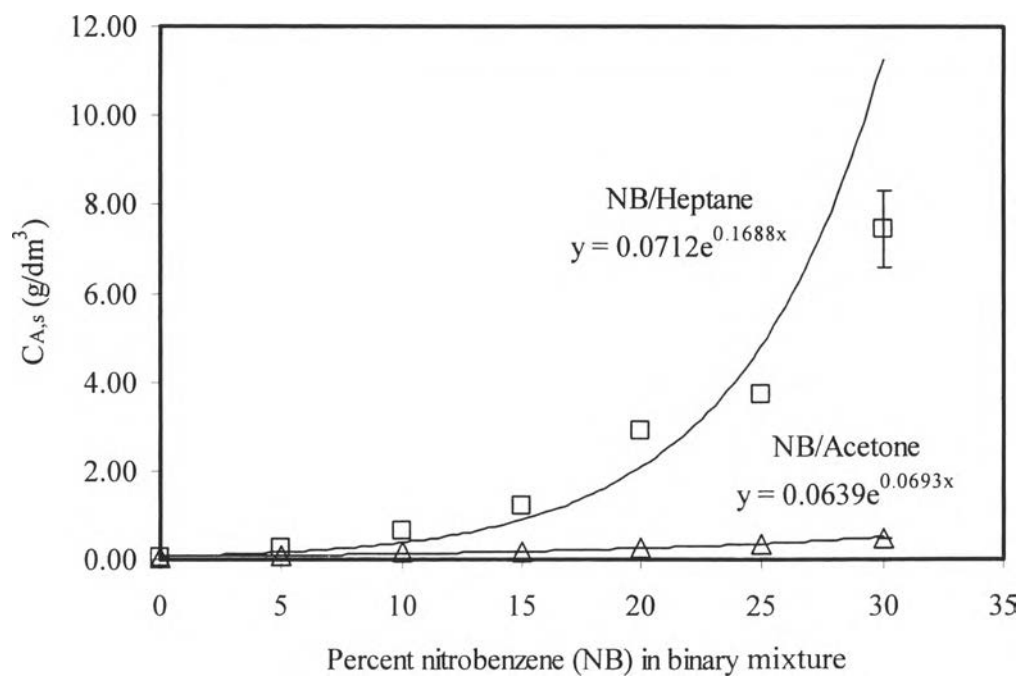


Figure 4.8 Solubility of unfractionated Cold Lake asphaltene in different solvent mixtures with nitrobenzene.

Table 4.6 Solvent volumes at the onset point of asphaltene precipitation

Binary solvents	Solvent volumes at onset point of asphaltene (ml)				
	F40/60*	F30/70*	F20/80*	F10/90*	Unfrac*
Toluene/Heptane	29.25	26.94	16.49	2.45	17.24
Toluene/Acetone	28.50	27.08	20.09	4.78	24.81
Toluene/Methanol	52.59	48.29	44.58	40.81	45.13
Toluene/Allyl Alcohol	30.58	32.37	30.26	16.91	27.59
Nitrobenzene/Acetone	32.31	28.11	27.38	7.28	19.68
Nitrobenzene/Heptane	-	-	-	-	7.44

*onset point of asphaltene is at $C_{A,s} = 0.25 \text{ g/dm}^3$

The solubility parameters at the surface of the Cold Lake asphaltene solubility spheroid can be estimated using the data in Table 4.6 and Equation (4.3) as shown below (Redelius, 2000).

$$\bar{\delta} = \frac{\phi_T \delta_{j,T} + \phi_S \delta_{j,S}}{\phi_T + \phi_S} \quad (4.3)$$

- where
- j = d, p or h
 - $\bar{\delta}$ = the solubility parameter at the surface of solubility space
 - $\delta_{j,T}$ = the solubility parameter of precipitant
 - $\delta_{j,S}$ = the solubility parameter of solvent
 - ϕ_T = the volume fraction of precipitant
 - = $\frac{V_T}{V_T + V_S}$
 - ϕ_S = the volume fraction of solvent
 - = $\frac{V_S}{V_T + V_S}$

V_T = the precipitant volume at the onset point of asphaltene precipitation, and
 V_S = the solvent volume at the onset point of asphaltene precipitation.

The solubility parameters at the surface of the Cold Lake solubility spheroids for both the unfractionated asphaltene and fractionated asphaltenes are summarized in Table 4.7.

Table 4.7 Solubility parameters at the surface of solubility spheroid the unfractionated Cold Lake asphaltene compare with those of fractionated asphaltene

Binary solvents	Solubility Parameters (MPa ^{0.5}) at the surface of solubility spheroid		
	δ_d	δ_p	δ_h
Unfractionated Cold Lake			
Toluene/Heptane	15.77	0.24	0.34
Toluene/Acetone	16.12	8.17	5.76
Toluene/Methanol	16.41	7.38	13.14
Toluene/Allyl Alcohol	16.70	8.21	12.72
Nitrobenzene/Acetone	16.39	10.05	6.43
Nitrobenzene/Heptane	15.65	0.64	0.31
F40/60 Fraction Cold Lake			
Toluene/Heptane	16.09	0.41	0.59
Toluene/Acetone	16.21	7.84	5.58
Toluene/Methanol	16.47	7.13	12.68
Toluene/Allyl Alcohol	16.75	7.93	12.27
Nitrobenzene/Acetone	16.95	9.82	6.06
F30/70 Fraction Cold Lake			
Toluene/Heptane	16.09	0.41	0.59
Toluene/Acetone	16.21	7.84	5.58

Toluene/Methanol	16.47	7.13	12.68
Toluene/Allyl Alcohol	16.78	7.76	12.01
Nitrobenzene/Acetone	16.76	9.89	6.18
F20/80 Fraction Cold Lake			
Toluene/Heptane	15.75	0.23	0.33
Toluene/Acetone	16.00	8.59	6.00
Toluene/Methanol	16.39	7.44	13.25
Toluene/Allyl Alcohol	16.74	7.96	12.32
Nitrobenzene/Acetone	16.73	9.91	6.21
F10/90 Fraction Cold Lake			
Toluene/Heptane	15.37	0.03	0.05
Toluene/Acetone	15.62	9.97	6.76
Toluene/Methanol	16.28	7.85	14.02
Toluene/Allyl Alcohol	16.50	9.21	14.30
Nitrobenzene/Acetone	15.83	10.27	6.79

Table 4.7 was used to construct the solubility spheroid of unfractionated and fractionated Cold Lake asphaltene. The solubility parameters of pure solvent and precipitants were also included in the 3-D plots to indicate asphaltene soluble and insoluble phases. The plots of the unfractionated and fractionated Cold Lake asphaltene solubility spheroids are given in Figures 4.9 to 4.13.

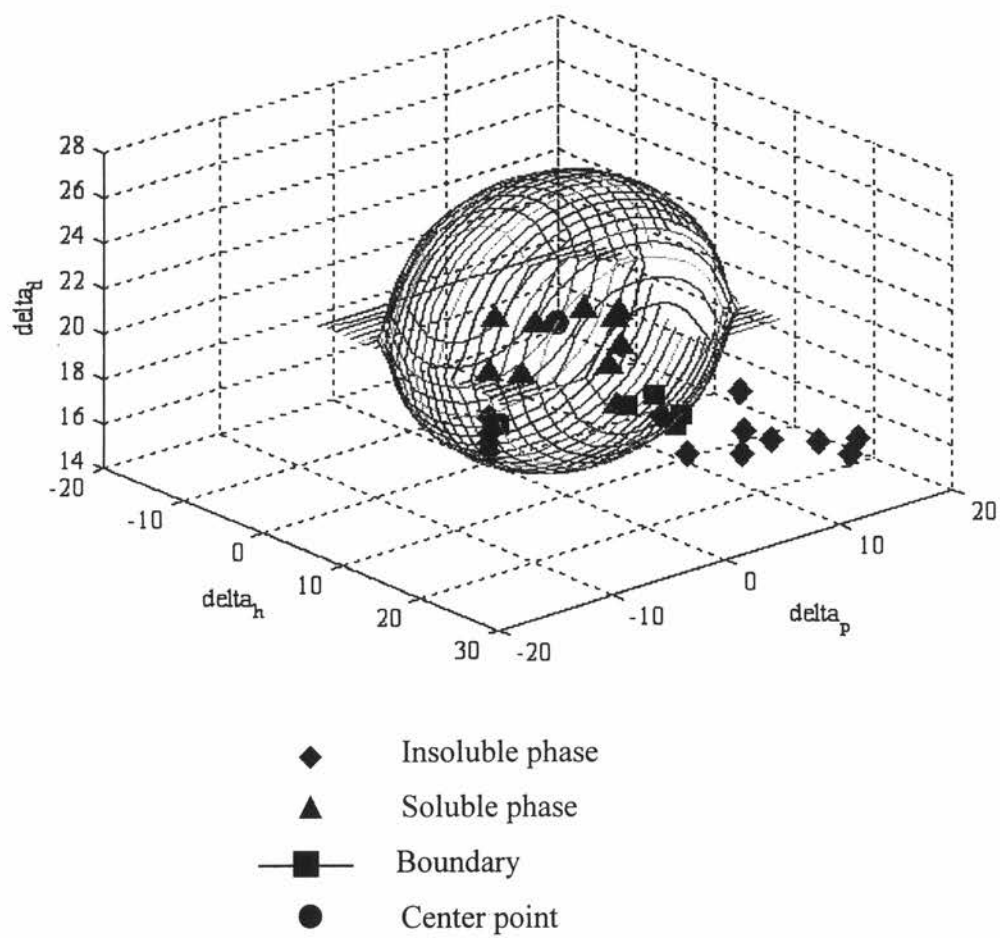


Figure 4.9 Solubility spheroid of unfractionated Cold Lake asphaltene.

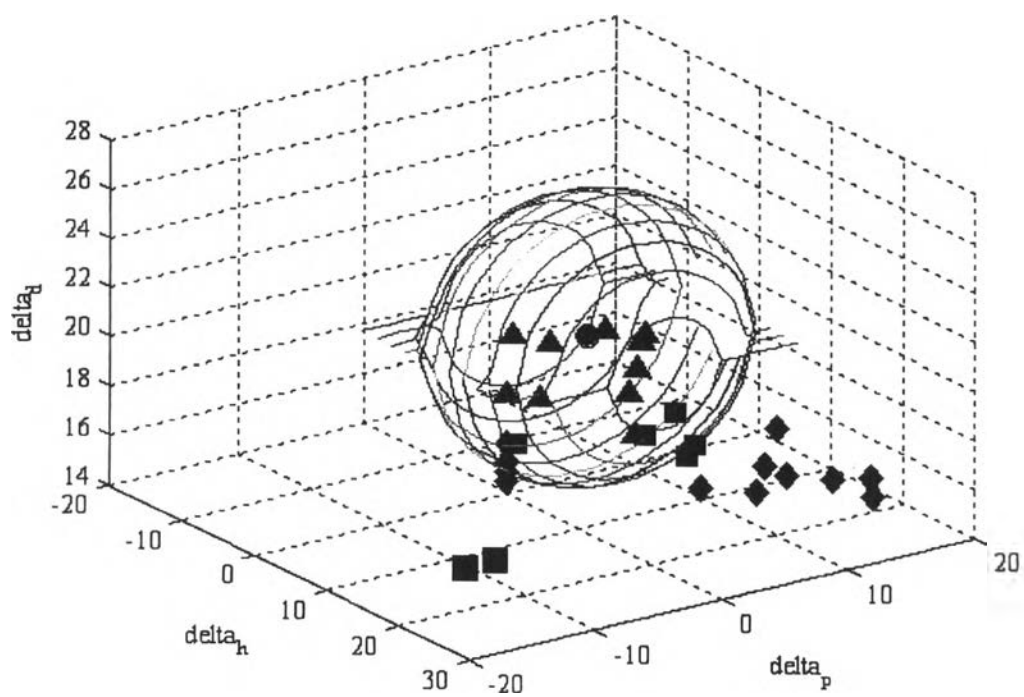


Figure 4.10 Solubility spheroid of F40/60 Fraction of Cold Lake asphaltene.

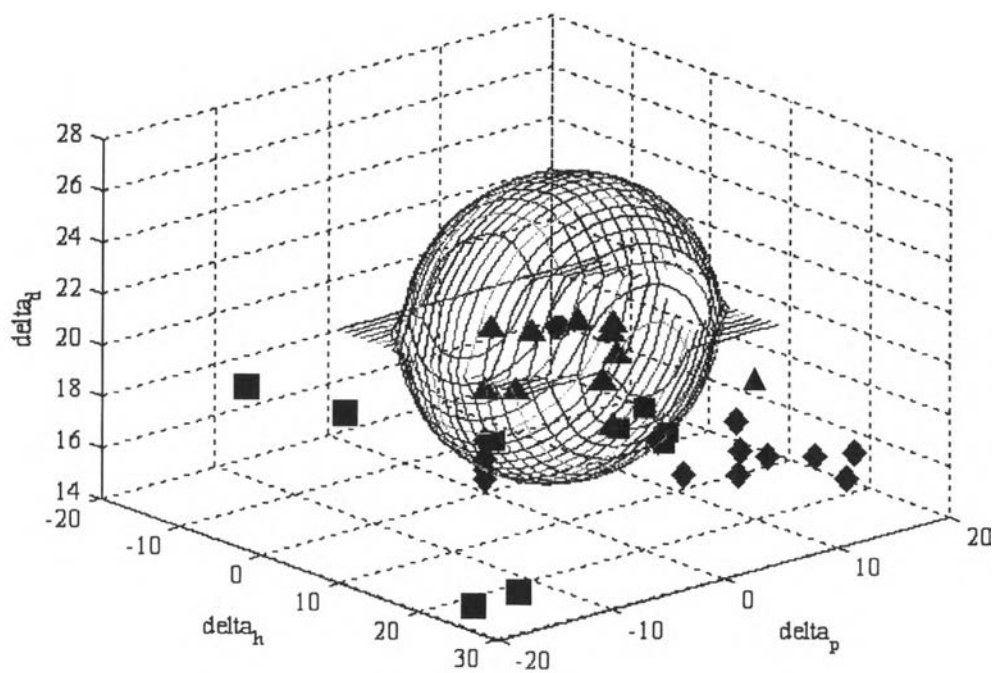


Figure 4.11 Solubility spheroid of F30/70 Fraction of Cold Lake asphaltene.

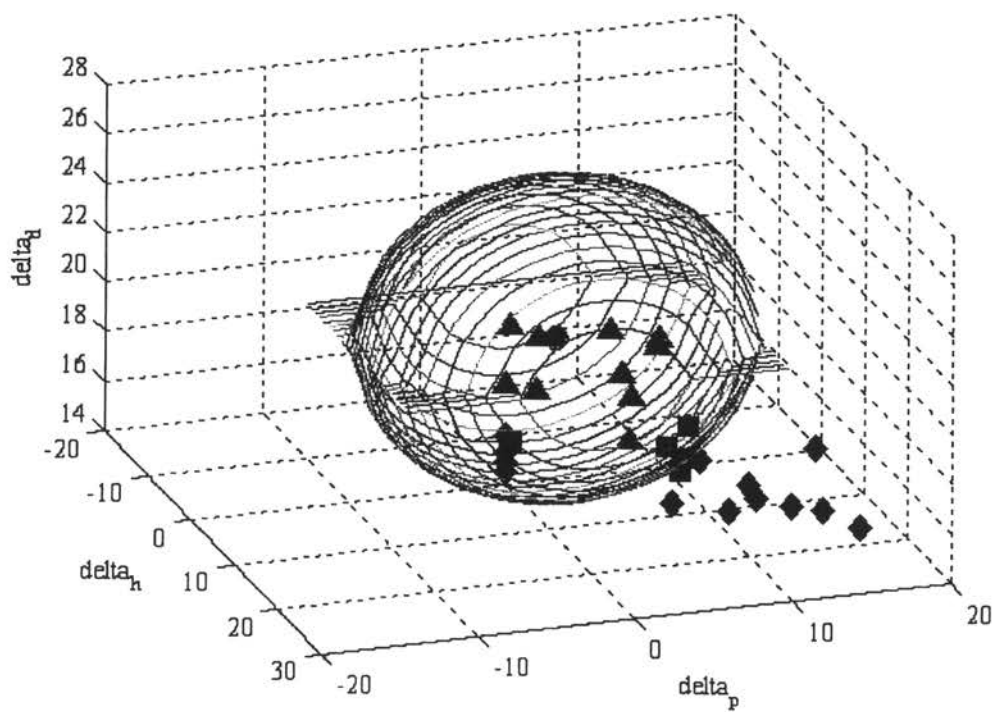


Figure 4.12. Solubility spheroid of F20/80 Fraction of Cold Lake asphaltene

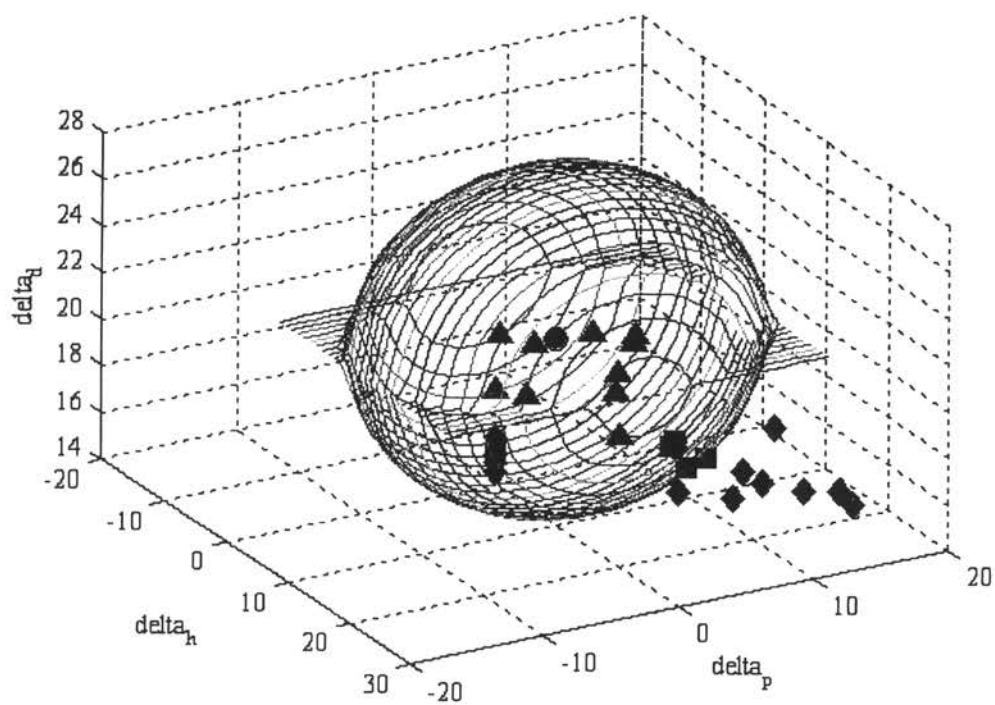


Figure 4.13. Solubility spheroid of F10/90 Fraction of Cold Lake asphaltene

The solubility parameters of unfractionated and fractionated Cold Lake asphaltenes are defined as the center point of the solubility spheroid. Since the dispersive solubility parameter ($\delta_{d,i}$) can be determined from the relation between the molar attraction constant (F_{di}), calculated from the group contribution method and molecular weight as shown in Figure 14.14 (Krevelen, 1976). The polar and hydrogen bonding solubility parameters can be predicted using solubility parameters at the boundary of solubility spheroids and spheroid equations which are shown in Appendix A. By using least square analysis and the appropriate constraints, which is obtained from fractionation procedure. The center point of asphaltene solubility spheroid or solubility parameters of unfractionated and fractionated Cold Lake asphaltene can be obtained and are shown in Table 4.8.

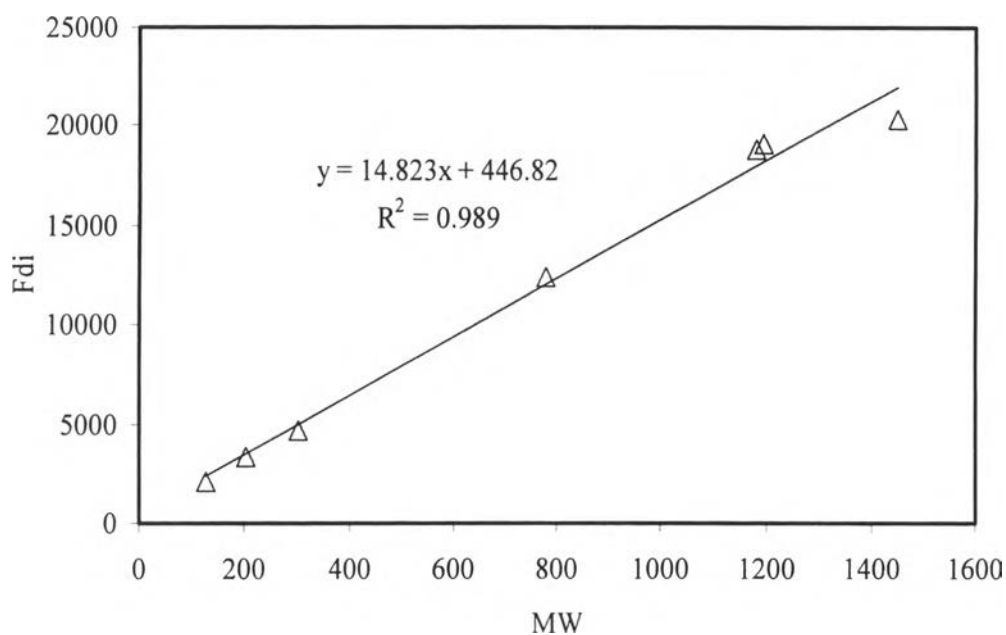


Figure 4.14 Relationship between molar attraction constant (F_{di}) and molecular weight.

Table 4.8 Solubility parameters of unfractionated and fractionated Cold Lake asphaltene

Asphaltene	Average Radius (R_d)	Solubility Parameters ($\text{MPa}^{0.5}$)		
		δ_d	δ_p	δ_h
Unfractionated Cold Lake	6.2353	21.12	1.0639	7.1159
F40/60 Fraction	5.7221	21.03	2.52	6.8631
F30/70 Fraction	5.8430	21.01	1.89	6.7212
F20/80 Fraction	6.2458	21.07	1.26	6.9906
F10/90 Fraction	7.0993	21.36	1.26	7.2806

As can be seen in Table 4.8, different fractions of asphaltenes have different value of solubility parameters.

4.6 Asphaltene Molecular Weight Prediction

The molecular weights of unfractionated Cold Lake asphaltene and its fractionated components are calculated using the single and three-component solubility parameter models (Equations (2.5) and (2.6)) with $\delta = 22.49 \text{ MPa}^{0.5}$ and the solubility parameters given in Table 4.12. The Cold Lake asphaltene molecular weights obtained from the three-component solubility model are higher than those from the single component solubility model as shown in Figure 4.15.

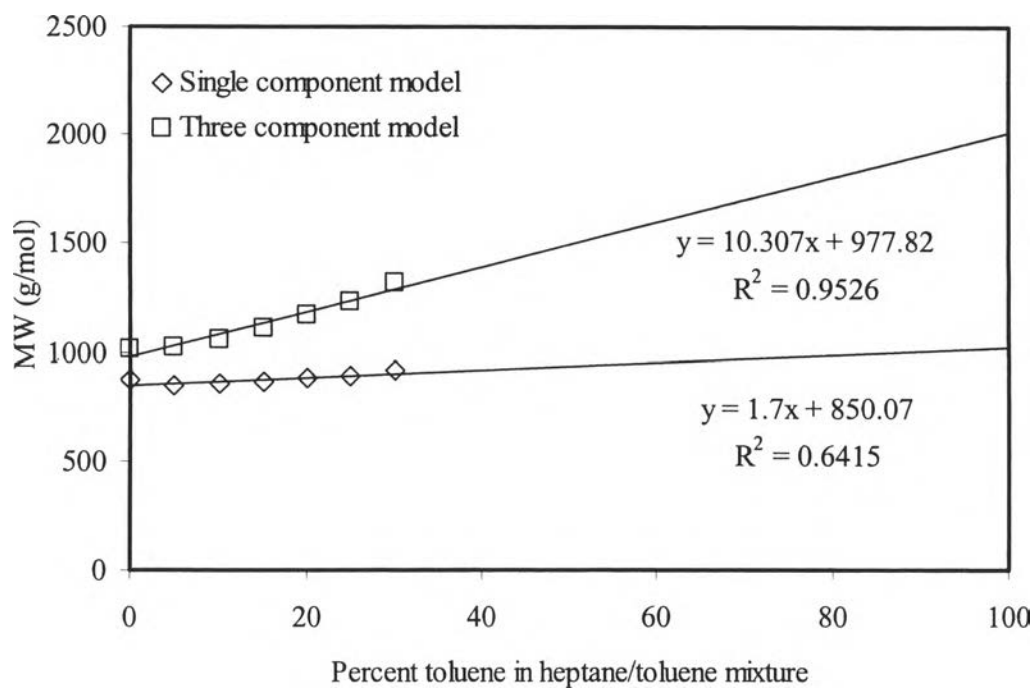


Figure 4.15 Relationship between the molecular weight of unfractionated Cold Lake asphaltene and percent toluene in heptane/toluene mixture.

The fractionated Cold Lake asphaltene showed the same trend. Figures 4.16 and 4.17 show the comparison of unfractionated and its fractionated Cold Lake asphaltene for single and three-component solubility parameter, respectively.

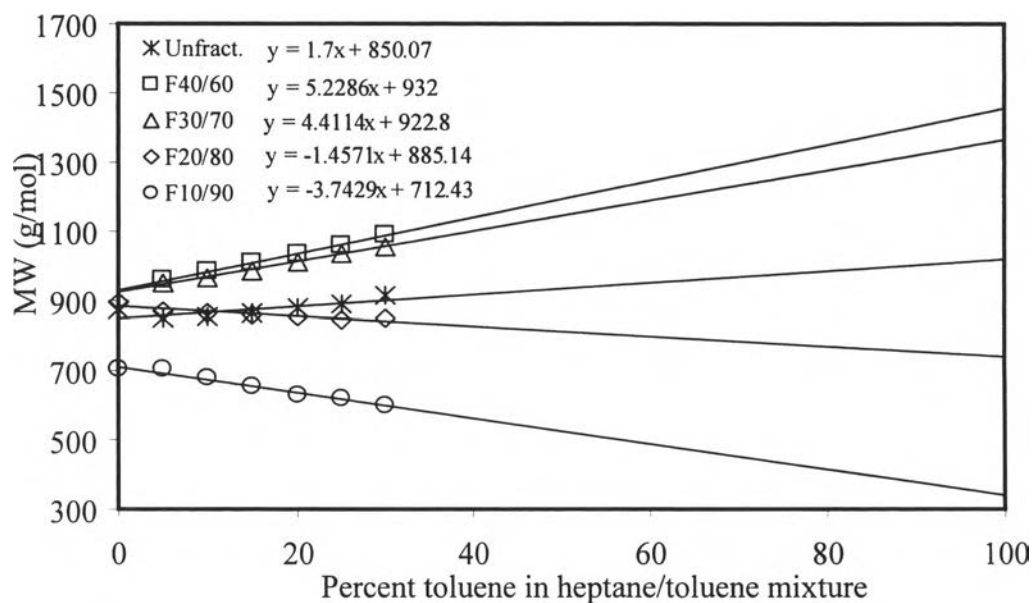


Figure 4.16 Comparison of the correlation between molecular weight and percent toluene in heptane/toluene mixture of all fractionated Cold Lake asphaltene for the single component solubility parameter model.

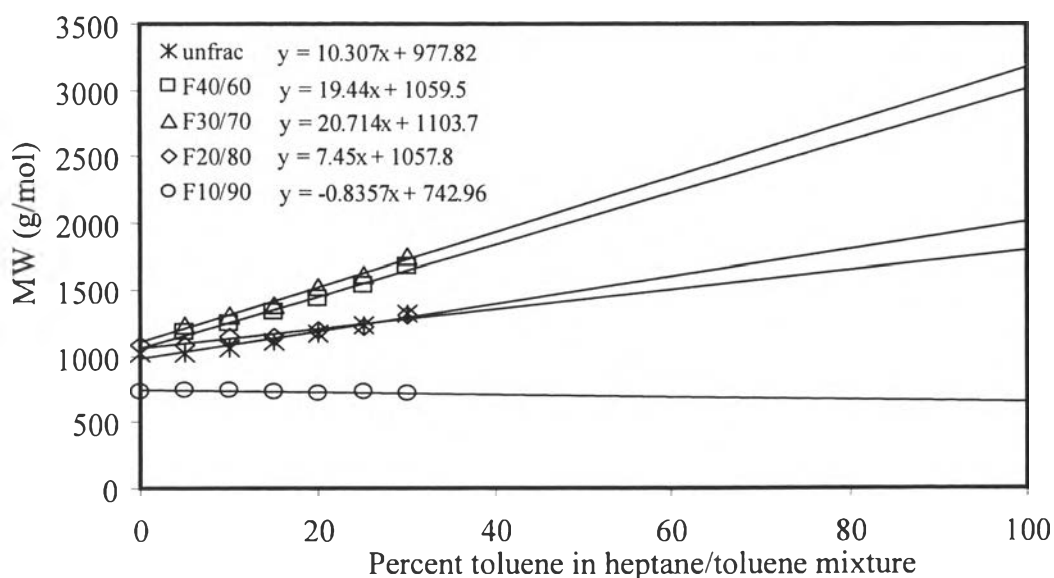


Figure 4.17 Comparison of the correlation between molecular weight and percent toluene in heptane of all fractionated Cold Lake asphaltene for the three-component solubility parameter model.

As can be seen in Figures 4.16 and 4.17, for the most part, the plots of the molecular weight as a function of the percent toluene in heptane of unfractionated and fractionated asphaltene have positive slopes. The molecular weight increased with increasing percent toluene in heptane except for the lowest polar fraction (F10/90). For the F10/90 Fraction, the molecular weight decreased with increasing percent toluene in heptane. One explanation is that the F10/90 Fraction contains more non-polar aliphatic branching components, corresponding to a lower polarity. Due to the very low polarity of the F10/90 molecules compared to the other fractions, the highest polar portion of the F10/90 Fraction, which its polarity is equivalent to the polarity of toluene, may dissolve first because the higher polar fractions have high molecular weights. The great molecular weights of the F10/90 Fraction were obtained at low percent toluene in heptane. Increasing the amount of solvent by increasing the percent toluene in heptane induced the dissolution of the lower polar molecule of F10/90, which had low molecular weight, and consequently resulted in the reduction of overall asphaltene molecular weight.

The molecular weights of Cold Lake asphaltenes are reported in Table 4.9 in terms of the upper and lower limits of average molecular weight shown in Figures 4.16 and 17. The molecular weight at a hundred percent toluene was defined as the upper limit of average molecular weight. On the other hand, the lower limit of average molecular weight was determined from the molecular weight at a hundred percent heptane.

Table 4.9 Predicted molecular weights of unfractionated and fractionated Cold Lake

Asphaltene	Predicted molecular weight					
	Single component model			Three-component model		
	0%Tol	10%Tol	100%Tol	0%Tol	10%Tol	100%Tol
Unfractionated Cold Lake	850	867	1020	978	1062	2009
F40/60 Cold Lake	932	983	1455	1060	1250	3004
F30/70 Cold Lake	923	963	1364	1104	1304	3175
F20/80 Cold Lake	885	864	739	1058	1150	1803
F10/90 Cold Lake	712	678	338	743	741	659

The predicted molecular weights from the three-component solubility parameters model are generally higher than those from the single component solubility parameter model. Asphaltene molecular weights increased with increasing the asphaltene polarity in both models. These results are consistent with the solubility results. The high polar fractions having high molecular weight are more difficult to be dissolved. Moreover, these predicted molecular weights are corresponding to the molecular sizes obtained from NMR measurement. The molecular sizes (diameter) of the highest polar fraction (F40/60) are 23 Å and 21 Å, 19 Å, 16 Å for F30/70, F20/80 and F10/90, respectively. It indicates that the high polar asphaltene molecules have high molecular sizes as expressed in Figure 4.18.

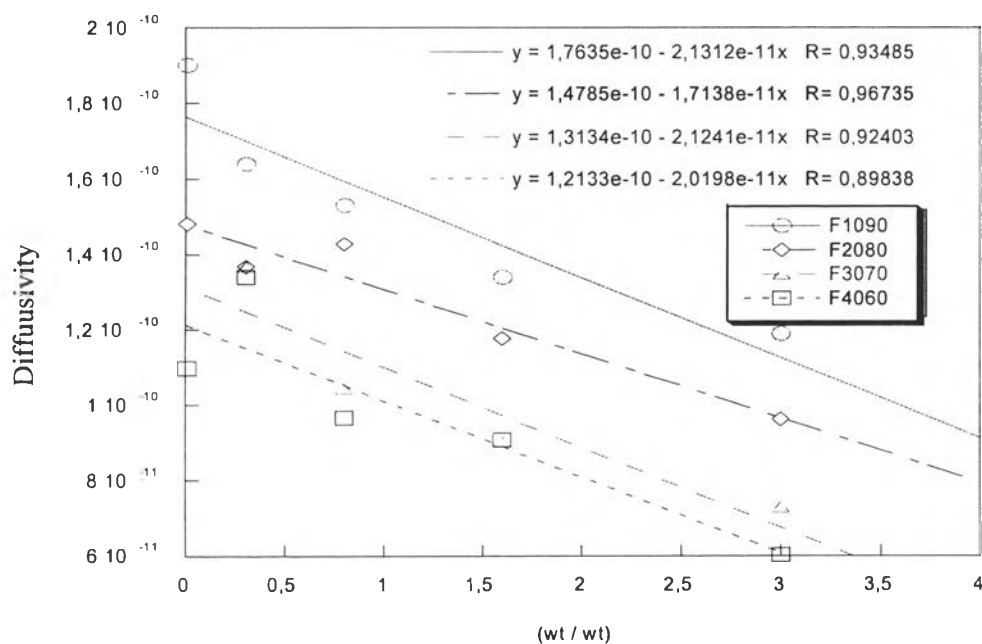


Figure 4.18 NMR-self diffusion of Cold Lake asphaltene.