# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Precipitation and Fractionation

Table 4.1 shows the SARA analysis for the compositions of two types of crude oils. The chemical compositions of the crude oils were supplied from PDVSA-Intervep company, Venezuela. NM1 crude oil contained much higher amount of asphaltene approximately 4 times higher than NM5. Experimentally, asphaltenes were precipitated out from these two crude oils using the method described in the previous chapter. The asphaltene precipitated from NM1 crude oil was shiny black and hard. It was different from the asphaltene precipitated from NM5 crude oil, which appeared to be a dark brown powder. Figure 4.1 shows the yields of two asphaltenes obtained from NM1 and NM5 crude oils. NM1 crude oil yielded about 90 gram of asphaltene per litre of crude while NM5 crude yielded 23 gram of asphaltene per litre of crude. The amount of asphaltene precipitated from NM1 crude was much greater than by a factor of approximately 4 times of the precipitate from NM5 crude. This maybe, in part, due to the large amount of high polar fraction asphaltenes in NM1 crude oil.

NM1 and NM5 asphaltenes were fractionated using the method described in Chapter II. Fractionation results of both NM1 and NM5 asphaltenes are shown in Figure 4.2. For both asphaltenes, the first fraction precipitated out at a ratio of 70/30 and thelast fraction precipitated out at ratio of 95/5 heptane/dichloromethane. NM1 asphaltene was mainly composed of the high polar fractions of F70/30 and F80/20. On the other hand, NM5 asphaltene was found to contain the high polar fraction of 54 percents of F80/20 and 6 percents of F70/30. That was why NM1 asphaltene was far more difficult to dissolve than NM5 asphaltene which contained less amount of the highest polar fraction as will be discussed in the next section.

Table 4.1 SARA analysis of two crude oils.

CrudeOil	Saturates (%)	Aromatics(%)	Resins (%)	Asphaltenes(%)
NM1	29.9	44.3	17.9	7.9
NM5	43.5	43.2	11.3	2
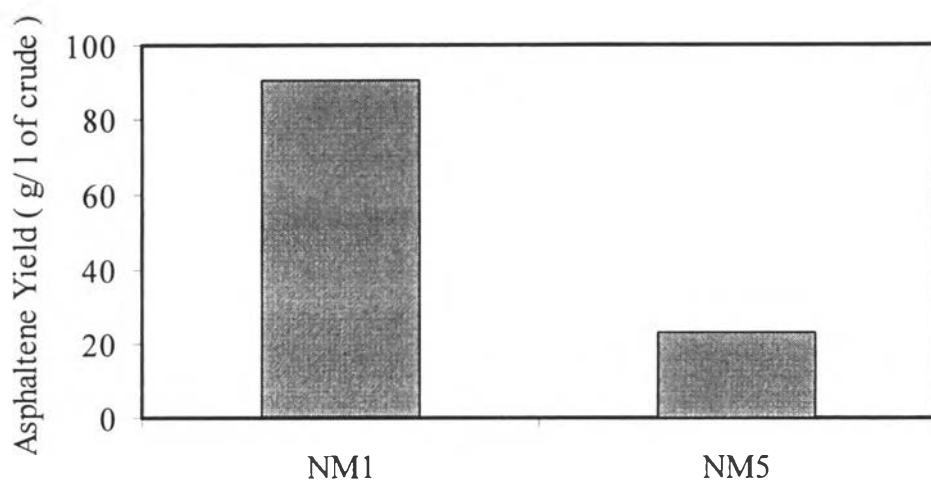
Figure 4.1 The asphaltene yields precipitated from two crude oils.
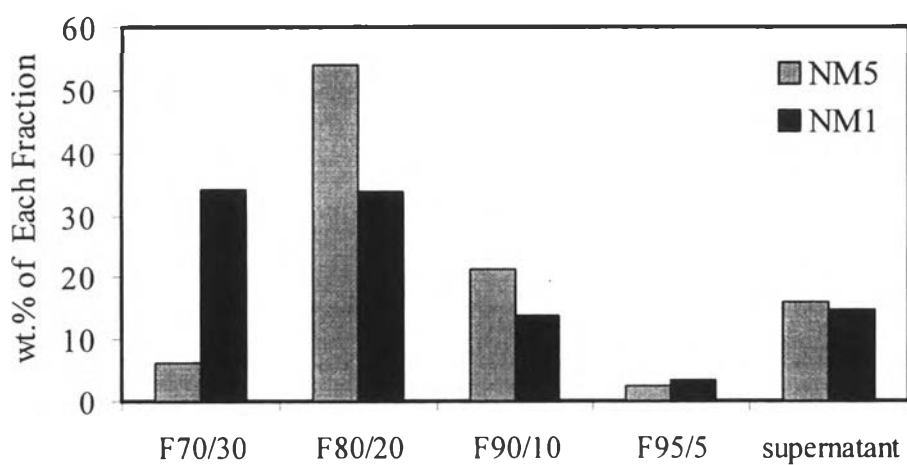
Figure 4.2 The fractionation yields of NM1 and NM5 asphaltenes.

Some amount of asphaltene remained in the supernatant because the original asphaltene sample was not washed with excess heptane after it was precipitated. Subsequently, some of the asphaltene sample was soluble in heptane. The physical appearance of the most polar fraction (F70/30) and the least of polar fraction (F90/10) differed dramatically. The F70/30 had a dark- black color and was shiny while the F90/10 was a dull-brown color and looked like a powder. Figure 4.3 shows the SEM images of F70/30 and F90/10 fractions of NM1 asphaltene. The morphologies of these two fractions were different. The fraction F70/30 appeared to have less surface area than the F90/10 did. Therefore the lower pseudo reaction rate constant of F70/30 might be regarding from its lower surface area.


F70/30   F90/10

F70/30   F90/10
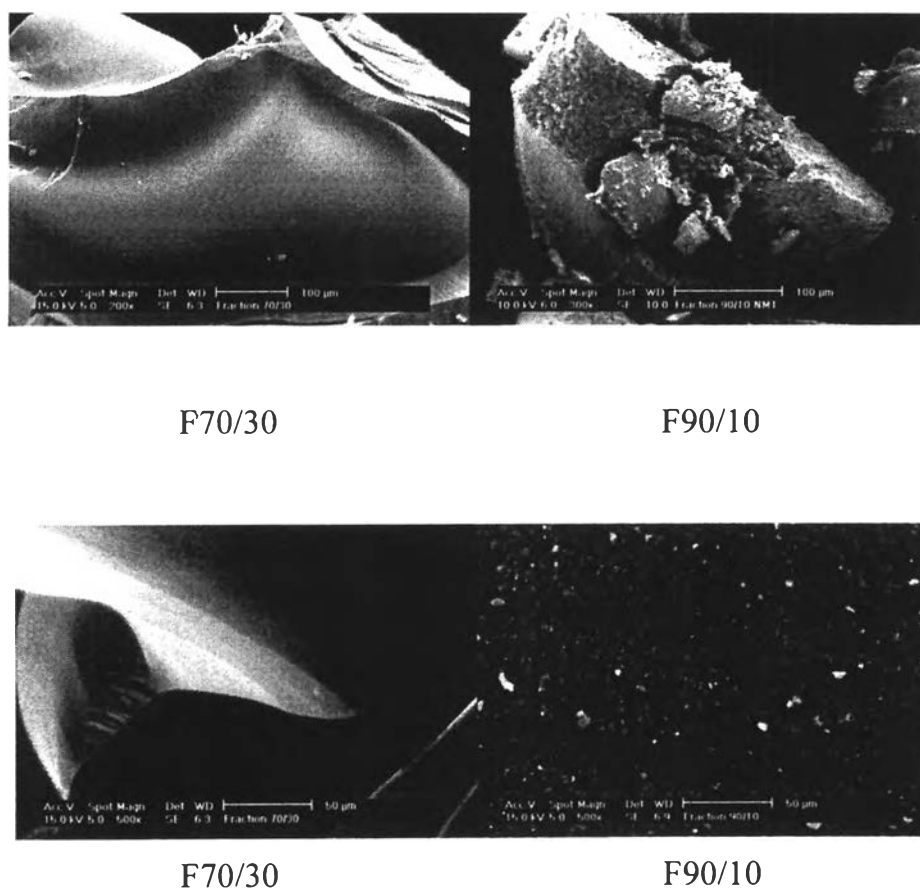
Figure 4.3 SEM images of F70/30 and F90/10 of NM1 asphaltenes.

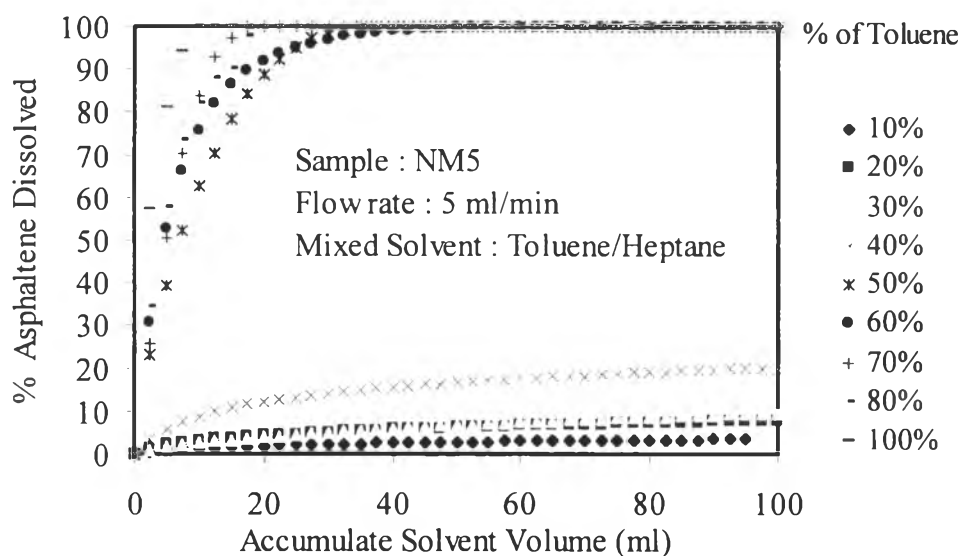## 4.2 Effect of Toluene Fraction in Solvent Mixture on Asphaltene Dissolution

Dissolution of asphaltene was carried out in the differential reactor as shown in Chapter III. A mixture of toluene and heptane was used as a solvent in this dissolution experiment. The percentage of toluene in the mixture was varied from 5 to 100 percent volume. The dissolution curves of unfractionated NM1 and NM5 asphaltenes using the mixed solvents having various percentages of toluene at a constant flow rate of 5 ml/min are shown in Figures 4.4 and 4.5 respectively. Both NM1 and NM5 asphaltenes had the similar dissolution profiles. The percentage of asphaltene dissolved increased remarkably with increasing in percent toluene in the mixed solvent. The dissolution profiles of both asphaltenes decreased substantially if the percentage of toluene was lower than 60% and 50% for NM1 and NM5 asphaltenes, respectively. Figure 4.6 shows the plot of percentage of unfractionated NM1 and NM5 asphaltenes dissolved after 100 ml of the mixed solvent having various percentages of toluene. At a relatively low percent toluene in solvent, both of asphaltene samples remained undissolved. The percentage of asphaltene dissolution of NM1 and NM5 asphaltenes drastically increased when 60 % vol and 50 % vol of toluene were used, respectively.

The data of the dissolution profiles as shown in Figures 4.4 and 4.5 were further analyzed to determine the kinetics of asphaltene dissolution. Assuming that the rate of dissolution of asphaltene is first order with respect to the undissolved asphaltene mass, the pseudo reaction rate constants for NM1 and NM5 aspahltene dissolution as a function of percent toluene in solvent mixture are shown in Figure 4.7. The pseudo reaction rate constant of NM1 asphaltene stayed approximately constant over a range of 5-50 % volume toluene then steeply increased in range of 50-70 % volume toluene. Above 70 % toluene in solvent mixture, the curve leveled off as it reached the solubility limit. The same phenomenon was observed in the case of NM5 aphaltene, except that the increase started at 45 % volume toluene.
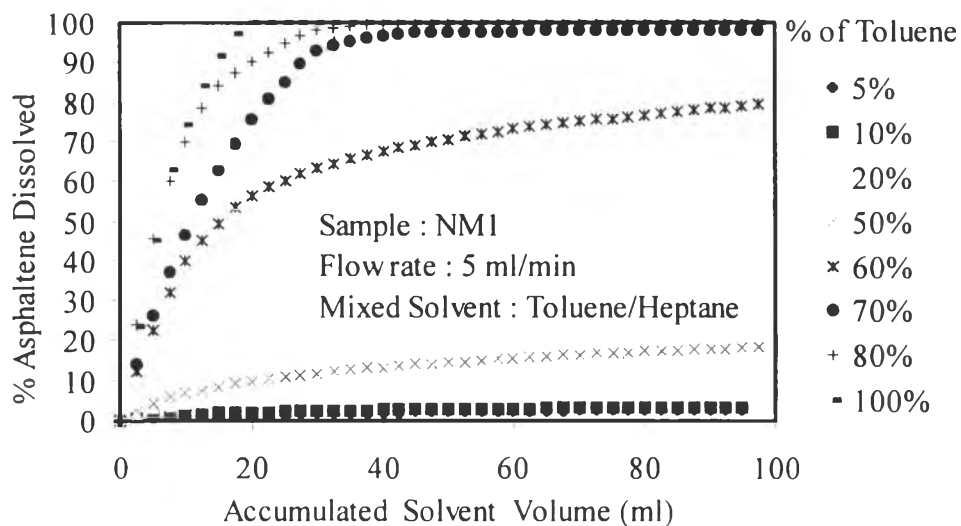
Figure 4.4 Dissolution profiles of unfractionated NM1 asphaltene using different percentages of toluene in solvent mixture.

Figure 4.5 Dissolution profiles of unfractionated NM5 asphaltene using different percentages of toluene in solvent mixture.
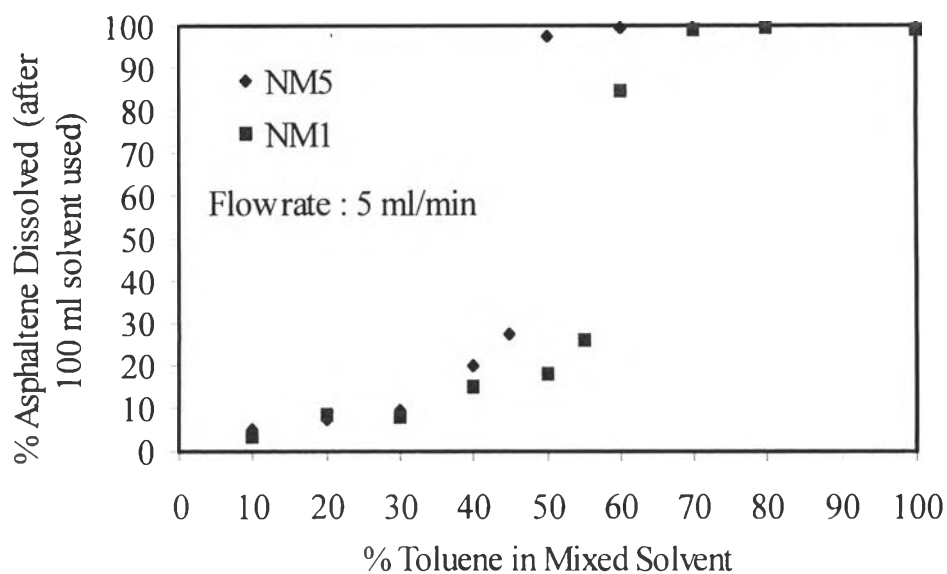
Figure 4.6 Percent asphaltene dissolved after 100 ml solvent used as a function of percent toluene in heptane of two unfractionated asphaltenes.
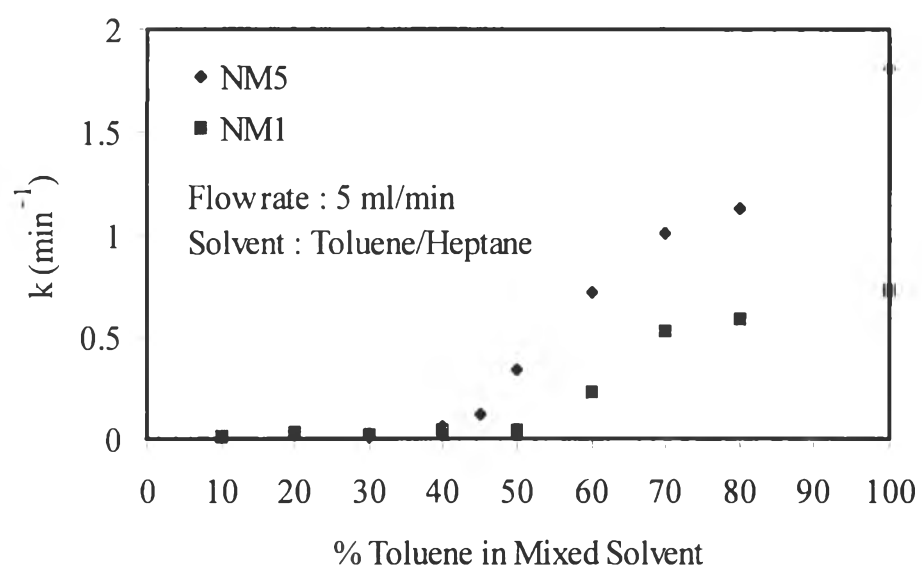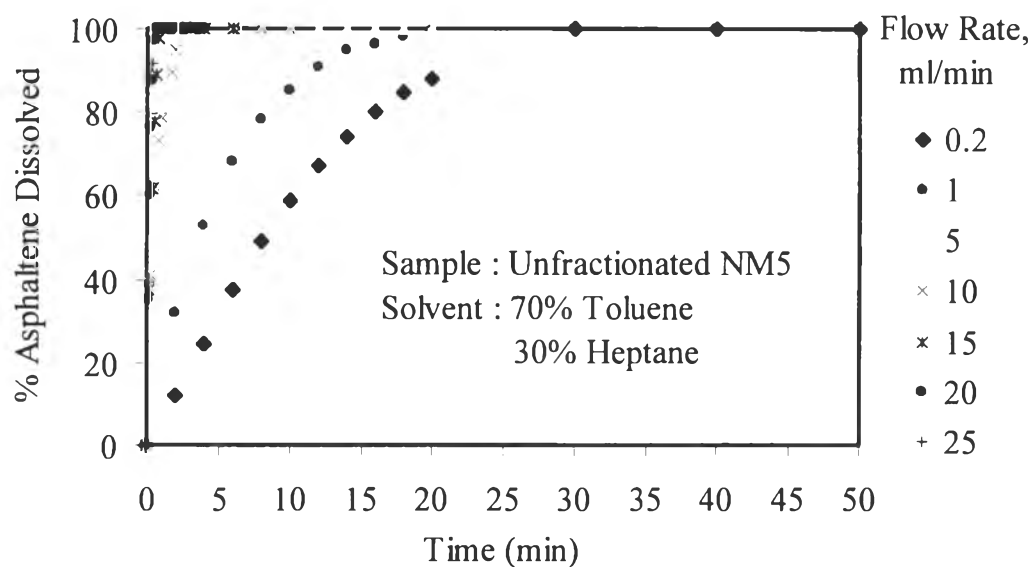

Figure 4.7 The pseudo reaction rate constant as a function of percent toluene in mixed solvent of two unfractionated asphaltenes.

4.3 Effect of Solvent Flow Rate on Asphaltene Dissolution

The effect of the flow rate of solvent mixture on the rate of asphaltene dissolution was studied using 70 % volume toluene in heptane. The profiles of asphaltene dissolution under different flow rates in the range of 0.2 to 30 ml/min are shown in Figure 4.8. The curves appeared much more closely overlapped for the flow rate higher than 5 ml/min. However, the asphaltene dissolution profiles at the low flow rate of solvent mixture i.e., 0.2 and 1 ml/min were more different from one to another.

The pseudo reaction rate constants of asphaltene dissolution can be simply calculated from the slopes of linear fitting to the initial [ln (M/Mo)] versus time for various flow rates as shown in Figure 4.9.
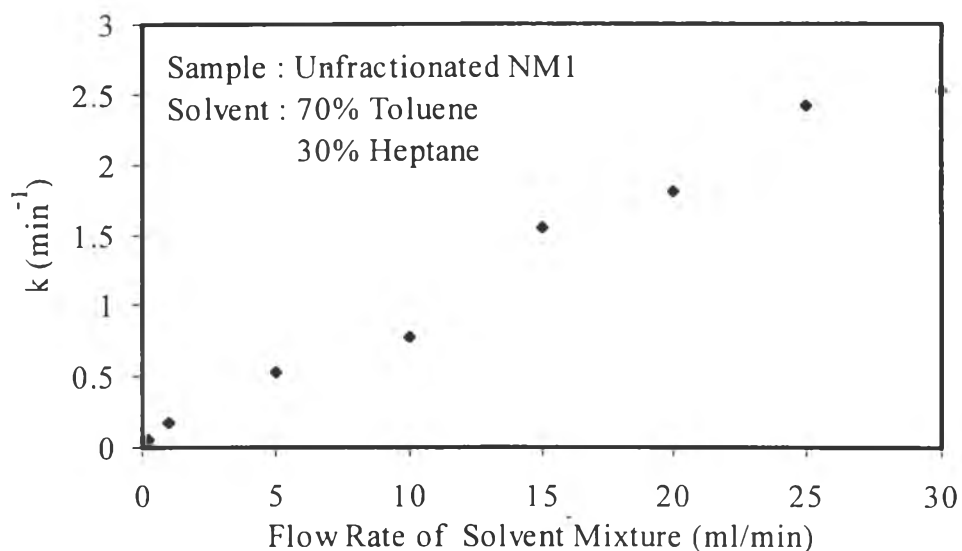

Figure 4.8 Evolution of asphaltene dissolved in 70% toluene as a function of flow rate.
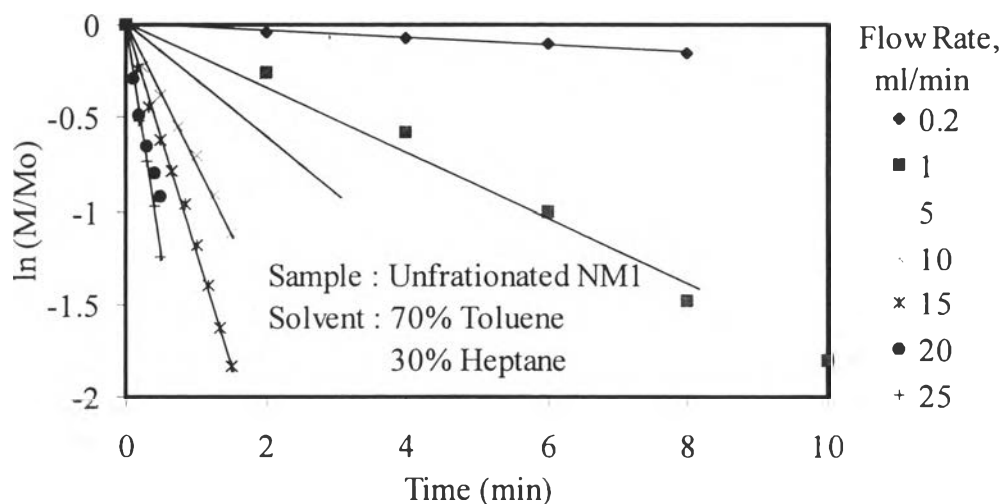
Figure 4.9 Kinetic analysis with first order reaction assumption for determining the pseudo reaction rate constant at different flow rates.

Figure 4.10 shows that the reaction rate constant of asphaltene dissolution almost linearly increased with increasing the flow rate in the range of 0.2 to 20 ml/min but it increased slower for the flow rate of toluene/heptane mixture above 20 ml/min. The increase in the pseudo reaction rate constant of asphaltene dissolution with increasing flow rate of fluid suggests that the convective mass transfer of species between the bulk fluid and the surface of asphaltene solid is a controlling factor in the rate of asphaltene dissolution. Increasing the solvent flow rate basically reduces the thickness of fluid boundary layer around the asphaltene particles and therefore enhances the rate of mass transfer ($k_c = D_{AB}/\delta$). However if the liquid velocity is sufficiently high, the mass transfer across the boundary layer no longer limits the rate of asphaltene dissolution. Under this relatively high flow rate of solvent mixture, the asphaltene dissolution rate becomes reaction-limiting.

Figure 4.10 Dissolution rate constant of unfractionated NM1 asphaltene as a function of flow rate.

4.4 Dissolution of Asphaltenes Having Different Polar Fractions

Studies of asphaltene dissolution were carried out on the unfractionated asphaltene powder and different polar fractions of NM1 asphaltene. 70 % volume toluene in heptane at a flow rate of 5 ml/min was used in this experiment. Figure 4.11 shows the asphaltenes dissolved as a function of accumulated volume. The most polar fraction of NM1 asphaltene, F70/30, was not completely dissolved even after passing 100 ml of accumulated solvent mixture. On the other hand, both the lower polar fraction and unfractionated asphaltene could be dissolved very quickly compared to the higher polar fractions. The results indicated that polarity of the asphaltene plays an important role in the rate of aspahaltene dissolution.
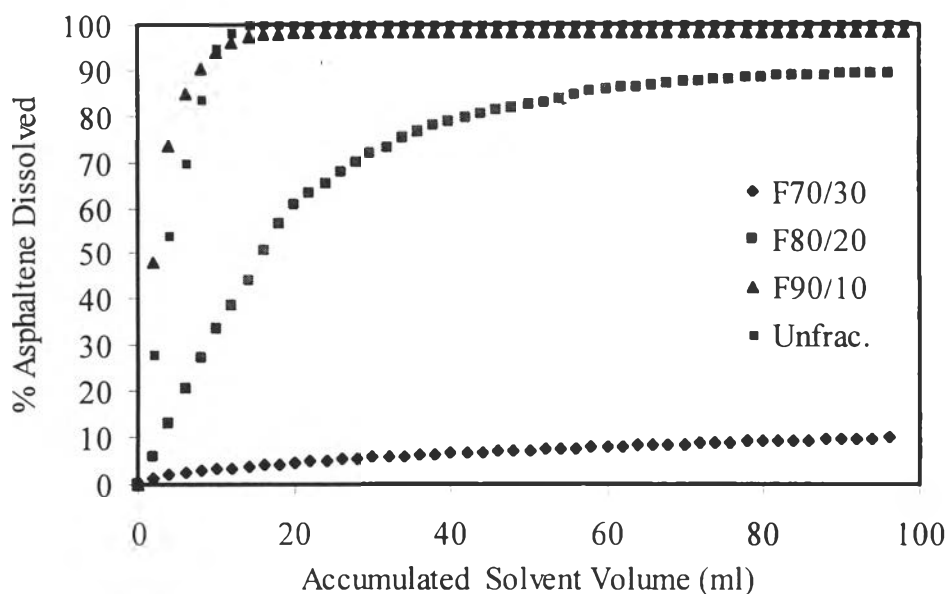
Figure 4.11 Dissolution profiles of fractionated and unfractionated NM1
asphaltene using 70% toluene in heptane.

Figure 4.12 shows determination of the rates of asphaltene dissolution using the first – order dissolution model for different polar fractions of NM1 asphaltene. The highest polar fraction (F70/30) was the most difficult to dissolve and therefore has the lowest value of k. Higher values of k can be obtained for F80/20, unfractionated, and F90/10 asphaltene, respectively. The two fractions of F70/30 and F90/10 displayed markedly different properties. F90/10, the least polar fraction, was reported to have the highest surface area (Nalwaya *et al.*, 1999).

It can be concluded that fractionation proves to be a powerful tool in determining the polarity of asphaltenes. If an asphaltene yields contain more of the higher polarity fraction (NM1), it means that the original asphaltene solid precipitated out from crude oil is more polar, and hence is more difficult to dissolve.
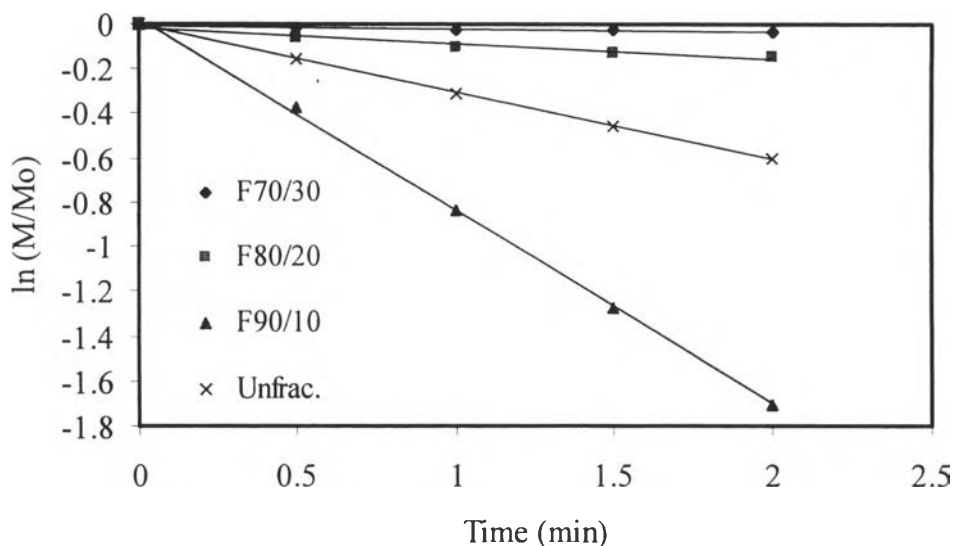
Figure 4.12 Kinetic analysis with first order reaction assumption for determining the pseudo reaction rate constants of different polar fractions of fractionated and unfractionated NM1 asphaltene.

4.5 Effect of Percent Toluene on Asphaltene Dissolution of Different Polar Fractions

The effect of percent toluene in solvent mixture on asphaltene dissolution of different polar fractions of NM5 asphaltene is shown in Figure 4.13. The experiments were conducted at a fixed flow rate of 5 ml/min and at room temperature of 22°C for different polar fractions of NM5 asphaltene. These experimental results illustrated that the higher polar fraction required a higher percentage of toluene for completele dissolution of asphaltene. The unfractionated asphaltene required 50 % toluene for complete dissolution, which was higher than the percentage of toluene required for the lower polar fractions of F90/10 and F 95/5. On the other hand, the more polar fraction, F80/20, required a higher percentage of toluene than the unfractionated asphaltene for complete dissolution. It is noticeable that the highest polar fraction, F70/30, could not be completely dissolved even pure toluene was used.
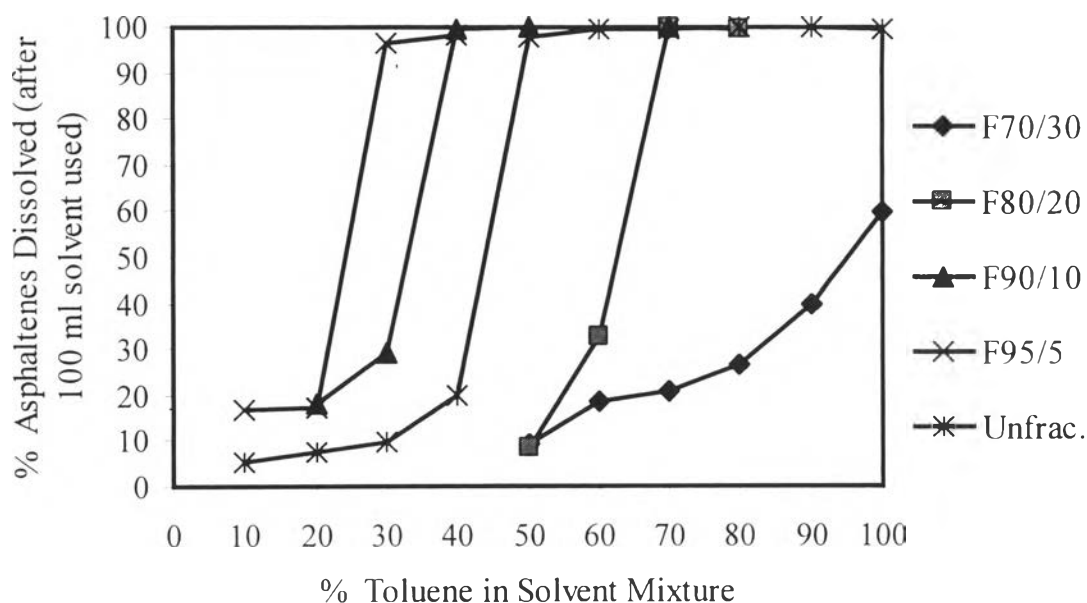
Figure 4.13 Percent asphaltene dissolved after 100 ml solvent used of
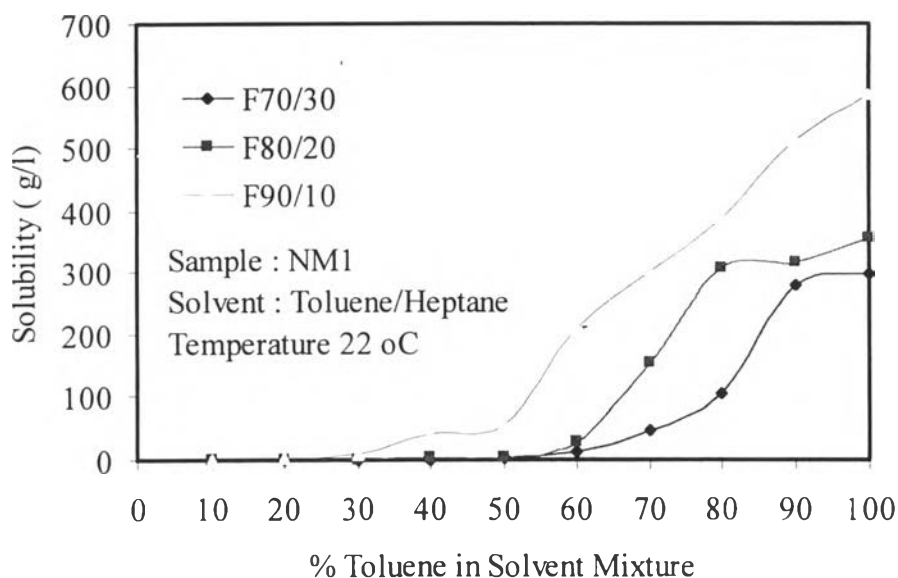different polar fractions of NM5 asphaltene.

4.6 Solubilities of Asphaltenes

In this study, the solubilities of NM1 and NM5 asphaltenes in various toluene/heptane solutions were measured in order to determine the effect of percent toluene in the solvent mixture on solubility of asphaltene. Figure 4.14 illustrates the solubilities of these two unfractionated asphaltenes in heptane media containing different percentages by volume of toluene. It was observed that the solubilities of both asphaltenes increased with increasing percent volume of toluene in the solvent mixture. The solubilities of asphaltenes stayed almost constant for toluene percentage lower than 50 % but beyond that point the solubilities of asphaltenes increased drastically with increasing toluene percentage. The solubility of NM5 asphaltene was relatively higher than that of NM1 for every toluene content in the solvent mixture, especially above 50 % toluene. This result can be explained by the effect of the polarity of asphaltene on solubility. The higher the polarity of asphaltene gave the lower the solubility value.
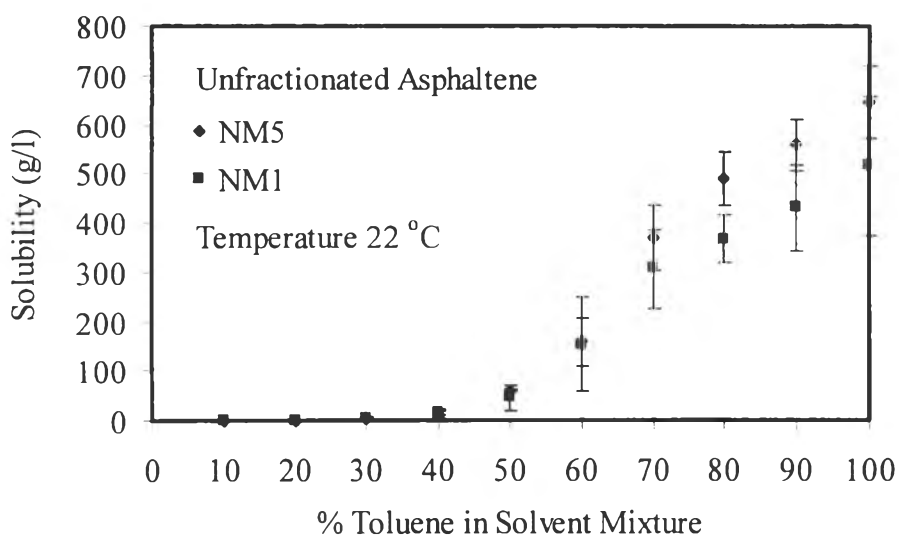
Figure 4.14 Solubilities of unfractionated asphaltenes as a function of
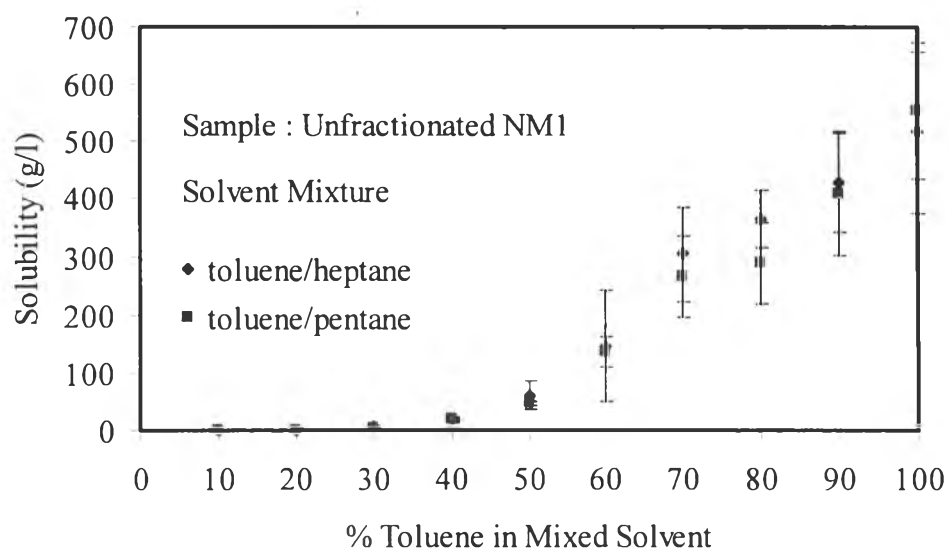percent toluene

Figure 4.15 shows the solubilities of different polar fractions of NM1 asphaltene. It was found that an increase in the asphaltene solubility was observed as the polarity of asphaltene decreased. The same as unfractionated asphaltenes, there were threshold percent volumes of toluene in solvent mixture needed for drastically increased in asphaltene solubility. Forty percent volume of toluene in solvent mixture was required to increase significantly the solubility of the least polar fraction, F90/10. As shown in Figure 4.15, there are not much difference in solubilities of all polar fractions for percent toluene lower than the threshold values. However, significant difference could be observed for percentage of toluene higher than the threshold values. It can be concluded that a higher percentage of toluene is required for complete asphaltene solubilization for a higher polar fraction.

Figure 4.15 Solubility of NM1 asphaltene as a function of percent toluene of different polar fractions.

4.7 Effect of Chain Length of Alkane Solvent on Asphaltene Solubility

The effect of alkane chain length on solubility of asphaltene was investigated using two types of alkane, heptane and pentane. The results given in Figure 4.16 show that the solubility of NM1 asphaltenes in toluene/heptane mixture was slightly higher than that in toluene/pentane mixture at any certain percent volume of toluene greater than 50 percent. The same trend for the value of the dissolution rate constant is observed from the dissolution studies carried out at a flow rate of 5 ml/min as shown in Figure 4.17. This can be explained by determining the correlation between amount of asphaltene precipitated and solvent properties i.e. solubility parameter (Anderson and Stenby, 1996). It was found that the amount of asphaltene precipitated tended to decrease as the number of carbons in the alkane solvent increased as changing from propane to heptane.
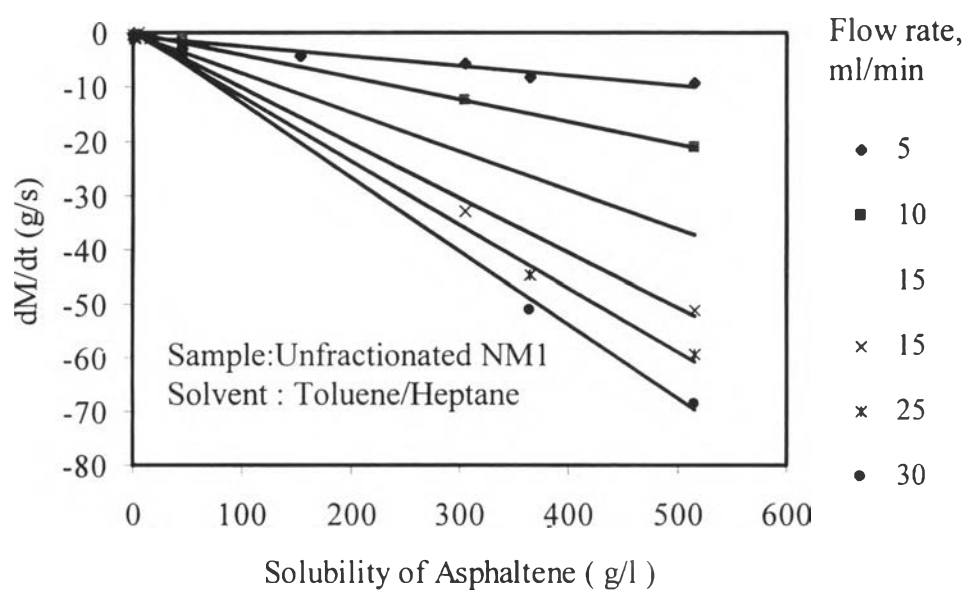
Figure 4.16 Solubilities of unfractionated NM1 asphaltene in toluene/heptane
and toluene/pentane at different percentages of toluene.
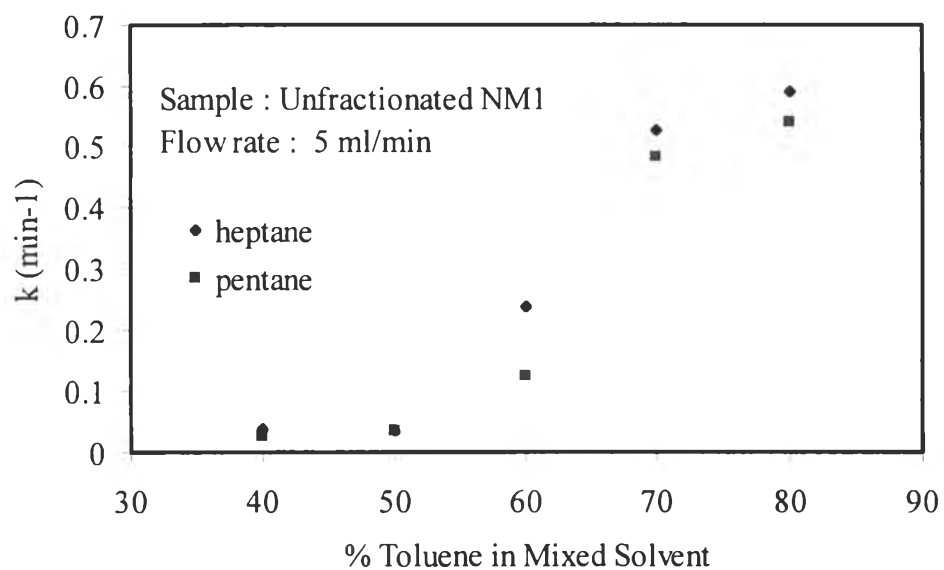
Figure 4.17 The pseudo reaction rate constants of unfractionated NM1
asphaltene dissolution as a function of percent toluene
in heptane and pentane.

4.8 Mass Transfer Coefficients of Asphaltenes

Asphaltene is considered to dissolve from its solid surface to bulk fluid. There is a high concentration of asphaltene in the fluid at the surface. This concentration, in general, is equal to the solubility of asphaltene in the solvent mixture. To learn the effect of solvent flow rate on the asphaltene dissolution rate, one needs to know how this parameter affects the mass transfer coefficient. From Equation 2.4, the mass transfer coefficient can be determined from the plot of dM/dt versus the solubility of asphaltene in different percentages of toluene in solvent mixture($C_{A S}$) as shown in Figure 4.18. All plots are straight lines whose slopes are the product of mass transfer coefficient and area. The bulk concentration is close to zero as shown from the intercept.


Figure 4.18 Plot of dM/dt versus solubility of unfractionated NM1 asphaltene at different flow rates using various percentages of toluene.

The product of mass transfer coefficient and area ($k_c A$) is plotted as a function of flow rate as shown in Figure 4.19. The $k_c A$ value increased almost linearly with increasing the flow rate; hence, the asphaltene dissolution using toluene/heptane mixture was mass transfer limited under the studied conditons. Here the specific dissolution rate constant is large with respect to the mass transfer coefficient. To increase the rate of asphaltene dissolution, one must increase C_{AS} and/or k_c as shown below;

$$-r_A'' \quad \alpha \quad k_c C_{AS} \tag{4.1}$$

For any given flow rate, the rate of asphaltene dissolution is basically controlled by the solubility or the concentration of asphaltene at the surface. The higher the percent toluene in the solvent mixture, the higher the solubility is, consequently, the higher the pseudo reaction rate constant is obtained.
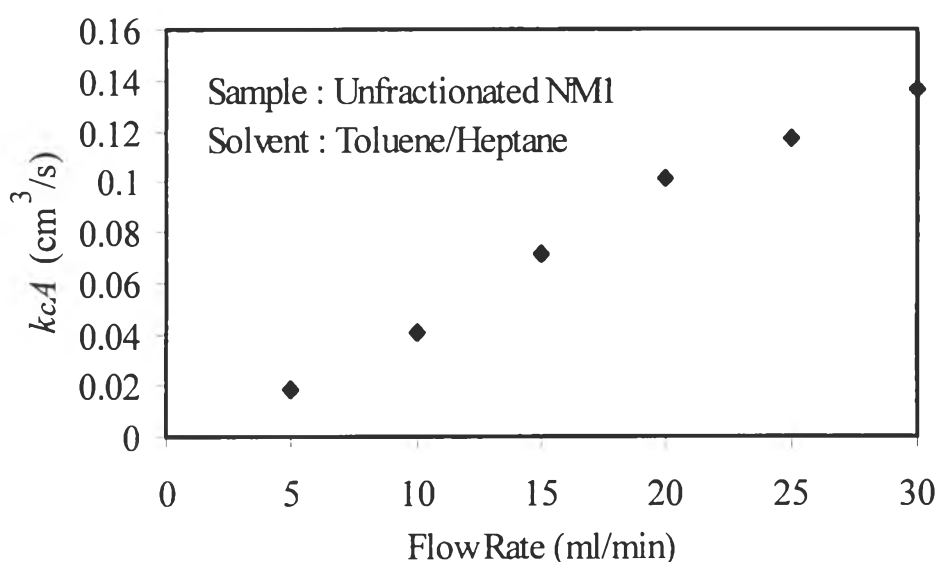
Figure 4.19 The relationship between $k_c A$ and flow rate of unfractionated NM1 asphaltene at different flow rates of solvent mixture.

4.9 Prediction of Asphaltene Solubility

To investigate whether an unfractionated asphaltene sample behaves as summation of its fractions, the solubility data updated for each of the fractions of both unfractionated asphaltenes of NM1 and NM5 were further analyzed. The calculated values of solubilities obtained from the summation of each fraction's solubility of NM1 asphaltene are then compared to the experimental solubility values of unfractionated NM5 asphaltene for different percent toluene in heptane as shown in Figure 4.20. It is a good correlation between the predicted and experimental solubilities suggesting that the unfractionated asphaltene samples do behave as the summation of their fractions.
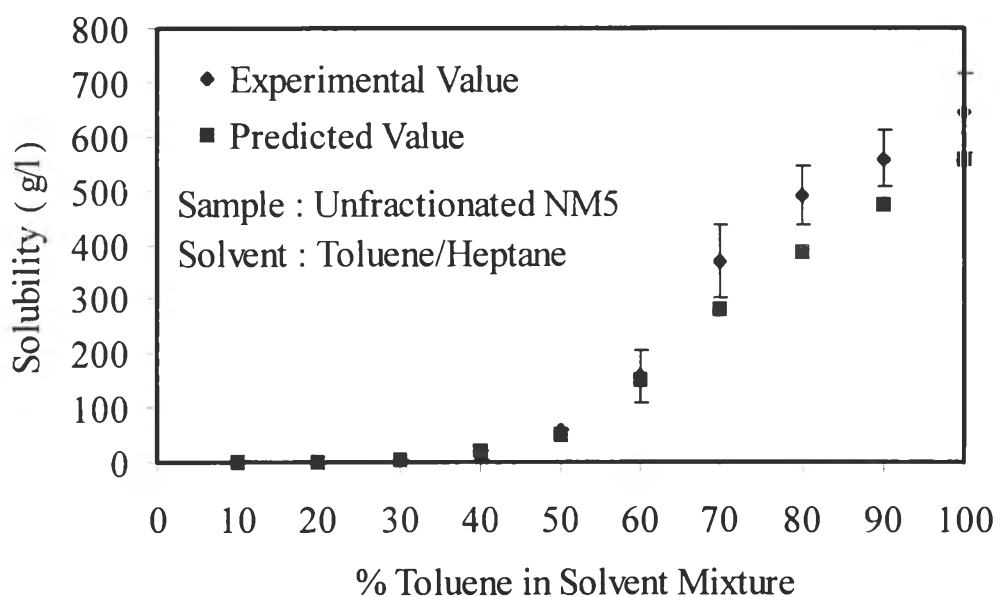

Figure 4.20 Comparison between the experimental values and the calculated values of solubilities of NM5 asphaltlenes at different percentages of toluene in heptane.

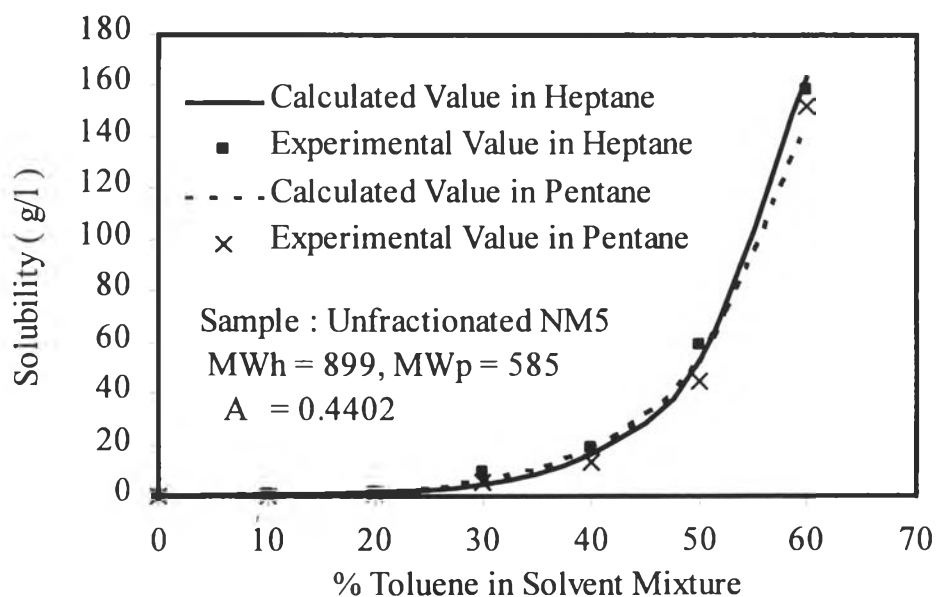## 4.10 Prediction of Molecular Weight of Asphaltene from Its Solubility
   ## Data

Solubilities of asphaltenes can be calculated from equilibrium ratios as shown in Equation 2.6 for single component solubility parameter. Asphaltene molar volumes and solubility parameter are estimated from Equations 2.7 and 2.8, respectively. Based on the experimental solubility data, the prediction of asphaltene molecular weight can be determined from Equation 2.10 using Solver mode in Microsoft excel.

The calculated and experimental solubility data of both NM1 and NM5 in two different solvents are plotted comparatively as shown in Figures 4.21 and 4.22, repectively. The calculated values fitted very well with the experimental data for the toluene content in solvent mixture lower than 60%. As discussed previously in Chapter II, the predicted molecular weight of asphaltene can be estimated from its solubility data. The predicted molecular weights of both asphaltenes (NM1 and NM5) in toluene/heptane are different from those in toluene/pentane. These results could be explained by self-aggregation behavior of asphaltenes in different solvents (Rogel et al., 2000). The higher the compatibility between asphaltenes and solvent (smaller value of difference in solubility parameters of asphaltene and solvent) leads to significantly larger asphaltene aggregate size in that particular solvent, and therefore, the larger predicted molecular weight is obtained. The predicted molecular weight of NM1 asphaltene was greater than that of NM5 asphaltene. This can be explained by relating to the solubility values and reaction rate constants; NM5 asphaltene solubilily was greater than that of NM1 asphaltene. Due to NM1 asphaltene contained more amount of the high polar fraction compare rate of NM5 aspahtene; therefore, NM1 asphaltene has higher predicted molecular weight than that of NM5 because of higher amount of heteroatom content in high polar fraction. From this result, NM1 asphaltene was far more difficult than NM5 asphaltene. The predicted molecular weight values fractions of NM1 asphaltene can be obtained from fitting the calculated and experiment solubility data of asphaltene in toluene/heptane mixtures as shown in Figures 4.23, 4.24, and 4.25 for
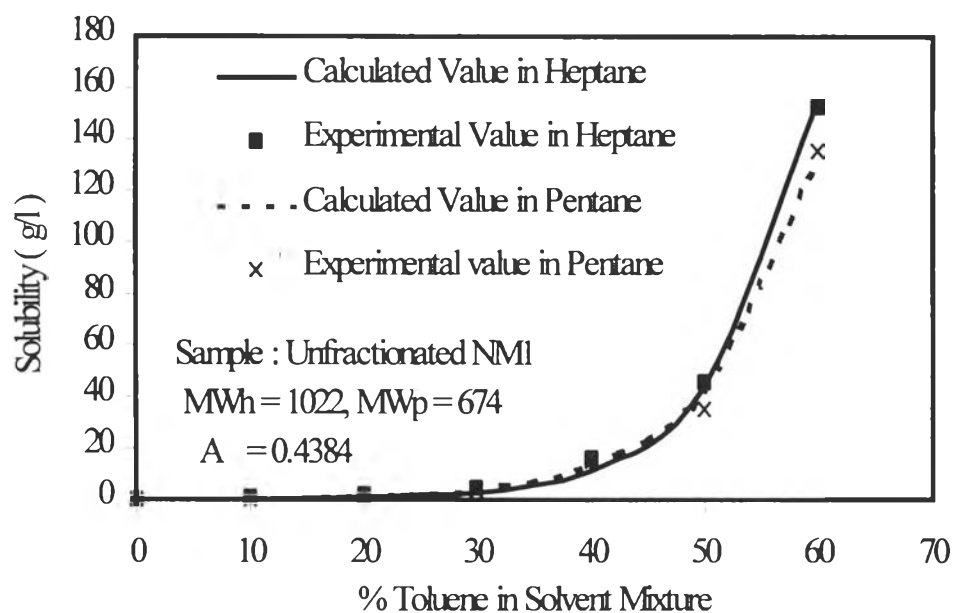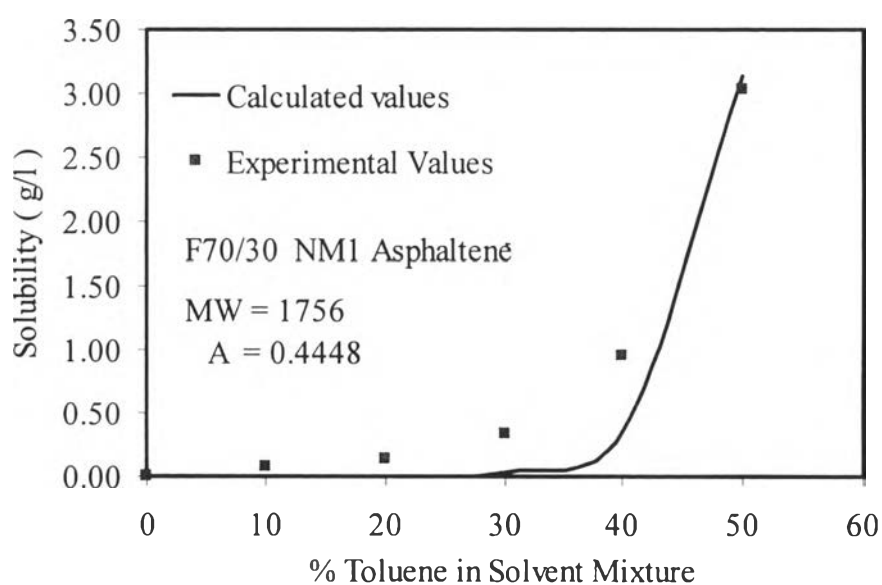
Figure 4.21 Predicted molecular weight of unfractionated NM1 asphaltenes calculated from solubility data.
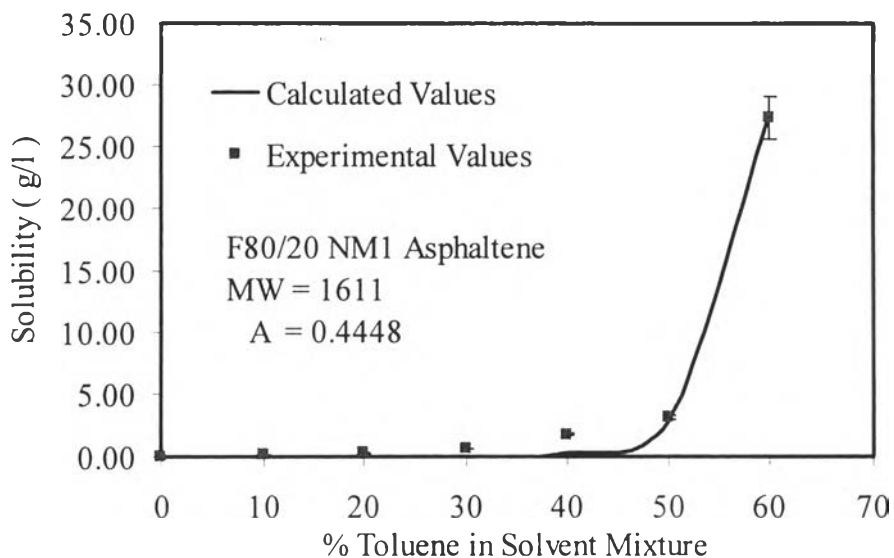

Figure 4.22 Predicted molecular weight of unfractionated NM5 asphaltenes calculated from solubility data.

F70/30, F80/20, and F90/10, respectively. The predicted values of molecular weights and the adjusting parameter(A) of unfractionated and fractionated asphaltenes were shown in Table 4.2. The predicted molecular weight increased as the polarity of asphaltene fraction increased. The results could be explained by the heteroatom content of the high polar fraction, which results in the high molecular weight value (Andersen, 1994).

Figure 4.23 Predicted molecular weight of F70/30 NM1 asphaltenes calculated from solubility data.

Figure 4.24 Predicted molecular weight of F80/20 NM1 asphaltenes calculalted from solubility data.
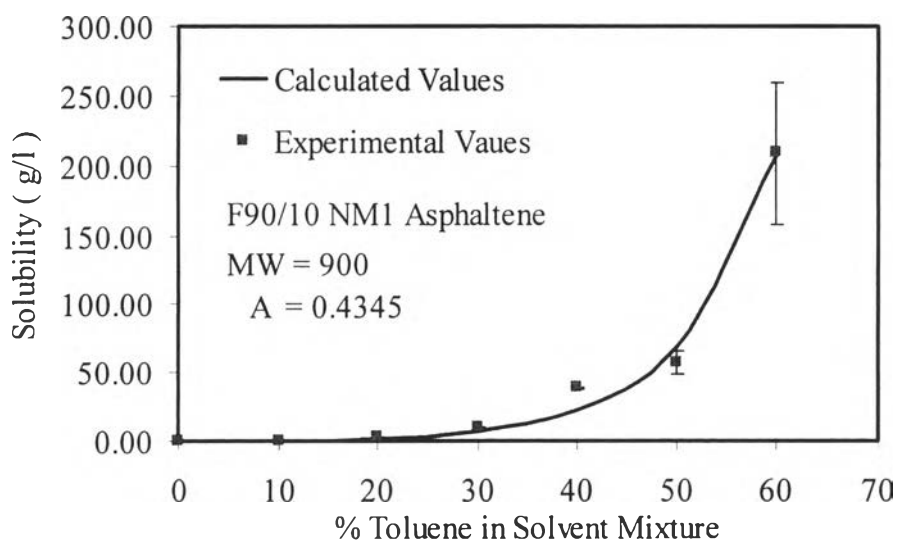
Figure 4.25 Predicted molecular weight of F90/10 NM1 asphaltenes calculated from solubility data.

Table 4.2 The predicted molecular weights of asphaltenes and adjusting

parameter A.

Asphaltene	A	Predicted Molecular Weight	
		Toluene/Heptane	Toluene/Pentane
Unfrac. NM5	0.4402	899	585
Unfrac. NM1	0.4384	1022	674
F70/30 NM1	0.4448	1756	-
F80/20 NM1	0.4448	1611	-
F90/10 NM1	0.4345	900	-