

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Scattering results

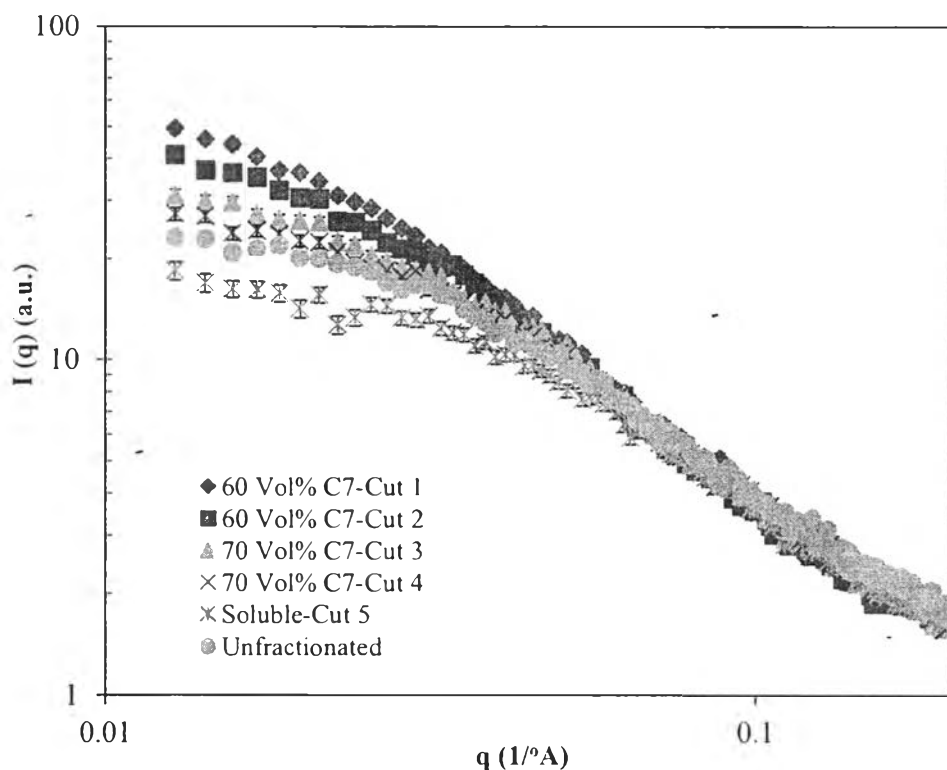
Asphaltenes govern self-association tendency to form nanometer- sized colloidal species, normally called as nanoaggregates, and disperse in solution. Discrepancy in size of asphaltene nanoaggregates is believed to correlate with asphaltene stability; the larger size of nanoaggregates is likely to have higher tendency to collide and stick with other surrounding aggregates forming larger clusters and eventually precipitate out of solution than smaller nanoaggregates. Therefore, utilizing small angle X-ray scattering to measuring the size of asphaltenes fractionated at different times and solubility can be used as a useful tool to determine the influence of asphaltenes' polydispersity on their stability. To investigate scattering characteristics among different fractionated asphaltenes, each fraction of fractionated A1 and K1 asphaltenes precipitated from two different asphaltene-content solutions as well as unfractionated A1 and K1 asphaltenes were separately dissolved in toluene to obtain 1 wt% asphaltene solutions. After being sonicated for 10 minutes and kept for 24 hours to allow the dissolution of asphaltenes in toluene, all model mixtures were then tested in optical microscope to verify their complete dissolution. The appearance of micron-sized particles or insoluble asphaltenes in each solution was not observed for fractionated A1 and K1 asphaltene samples, except the cut 1 extracted from both 3 wt% and 8 wt% solutions of K1 asphaltenes indicating that first fractions precipitated out of solution contain the most unstable asphaltenes. These first fractions of K1 asphaltene solutions were then centrifuged at 14000 rpm for 10 minutes to remove insoluble asphaltenes remaining in solution which approximately accounted for 4.75 wt% and 2.16 wt% of initial amount of asphaltenes for the samples extracted from 3 wt% and 8 wt% solutions, respectively. Figure 4.1 and 4.2 illustrate scattering intensity ( $I$ ) of fractioned A1 and K1 asphaltenes extracted from 3 wt% solutions as a function of scattering vector ( $q$ ), respectively. Scattering profiles for both types of asphaltenes indicated that there is a

variation in scattering characteristics of asphaltene fractions and scattering profiles of unfractionated asphaltenes lie on among fractionated asphaltenes' profiles.

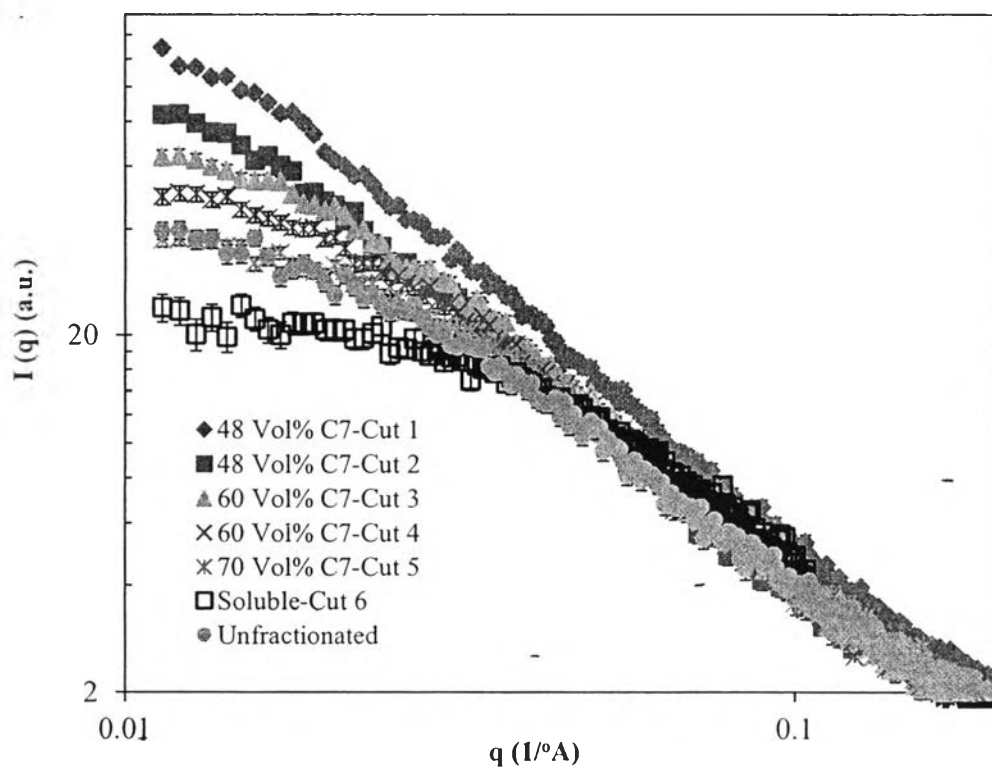
This result emphasizes the presence of polydispersed nature of asphaltenes. To compare the stability of each fraction, Guinier approximation, as shown in equation 4.1, was used to estimate the size of nanoaggregates for all fractions.

$$I(q) = I_0 \exp\left(-\frac{q^2 R_g^2}{3}\right) \quad \text{Eq. 4.1}$$

where  $I$  is scattering intensity which is a function of scattering vector ( $q$ ),  $I_0$  is the scattering intensity extrapolated at  $q=0$ ,  $q$  is scattering vector ( $1/\text{Å}$ ) and  $R_g$  is the radius of gyration ( $\text{Å}$ ).



**Figure 4.1** Scattering profile of unfractionated A1 asphaltenes and fractionated A1 asphaltenes extracted from 3 wt% asphaltene solution.



**Figure 4.2** Scattering profile of unfractionated K1 asphaltene and fractionated K1 asphaltene extracted from 3 wt% asphaltene solution.

Table 4.1 and 4.2 show the radius of gyration of A1 and K1 asphaltene fractions extracted from different asphaltene solutions. It can be clearly seen that the size of nanoaggregates decreases monotonically with increasing in time and heptane concentrations. Asphaltenes usually have their own thermodynamic solubility. According to their complex polydispersity, the higher precipitant concentrations have stronger destabilization power to precipitate more amounts and wider stability range of asphaltene compared to the lower precipitant concentrations. In addition, the most unstable asphaltene, which are believed to comprise of the most unstable constituents (e.g. large molecular weight, high metal content), are expected to precipitate out of solution first at low heptane concentrations. The estimated radius of gyration shows that all Cut 1 from A1 and K1 asphaltene, which are the earliest precipitated fractions from the lowest heptane concentration, form the largest nano-sized particles. Whereas, the latter precipitated fractions from identical heptane concentration, denoted as Cut 2, form the smaller nanoaggregates.

**Table 4.1** Radius of gyration of unfractionated and fractionated A1 asphaltenes extracted from 3 wt% and 8 wt% asphaltene-content solutions

1 wt% A1 Asphaltene fractions		Radius of Gyration (nm)	
		Extracted from 3 wt% Solution	Extracted from 8 wt% Solution
60 Vol% C7	Cut 1	$6.01 \pm 0.38$	$6.07 \pm 0.28$
	Cut 2	$5.69 \pm 0.33$	$5.07 \pm 0.23$
70 Vol% C7	Cut 3	$4.99 \pm 0.26$	$4.55 \pm 0.20$
	Cut 4	$4.14 \pm 0.16$	$3.96 \pm 0.16$
Soluble	Cut 5	$2.99 \pm 0.09$	$2.69 \pm 0.08$
Unfractionated Asphaltenes		$3.51 \pm 0.12$	

**Table 4.2** Radius of gyration of unfractionated and fractionated K1 asphaltenes extracted from 3 wt% and 8 wt% asphaltene-content solutions

1 wt% K1 Asphaltene fractions		Radius of Gyration (nm)	
		Extracted from 3 wt% Solution	Extracted from 8 wt% Solution
48 Vol% C7	Cut 1	$8.61 \pm 0.57$	$8.09 \pm 0.36$
	Cut 2	$8.32 \pm 0.46$	$7.56 \pm 0.31$
60 Vol% C7	Cut 3	$6.07 \pm 0.26$	$5.81 \pm 0.20$
	Cut 4	$5.74 \pm 0.39$	$5.46 \pm 0.17$
70 Vol% C7	Cut 5	$4.92 \pm 0.19$	$4.00 \pm 0.11$
Soluble	Cut 6	$2.78 \pm 0.10$	$2.32 \pm 0.13$
Unfractionated Asphaltenes		$4.51 \pm 0.30$	

For different heptane concentrations, the fractions precipitated from higher heptane concentrations (i.e. Cut 3 and Cut 4) form smaller nano-sized particles compared to the ones precipitated from lower heptane concentrations (i.e. Cut 1 and Cut 2). The last fractions, which are referred to Cut 5 for A1 asphaltenes and Cut 6 for K1 asphaltenes, precipitated from the highest heptane concentration associate into the smallest nanoaggregates. This result indicates that asphaltenes precipitated from different times and solubilities have different properties in terms of their sizes which are believed to influence on their stability. In addition, it was observed that all fractions of asphaltenes precipitated from 8 wt% asphaltene-content solution form the smaller nano-aggregates than fractions extracted from 3 wt% asphaltene-content solution. This implies that difference in asphaltene concentrations exhibit difference in polydispersity of asphaltenes and fractions from higher asphaltene-content solution are likely to have more stability than the ones from lower asphaltene-content solution.

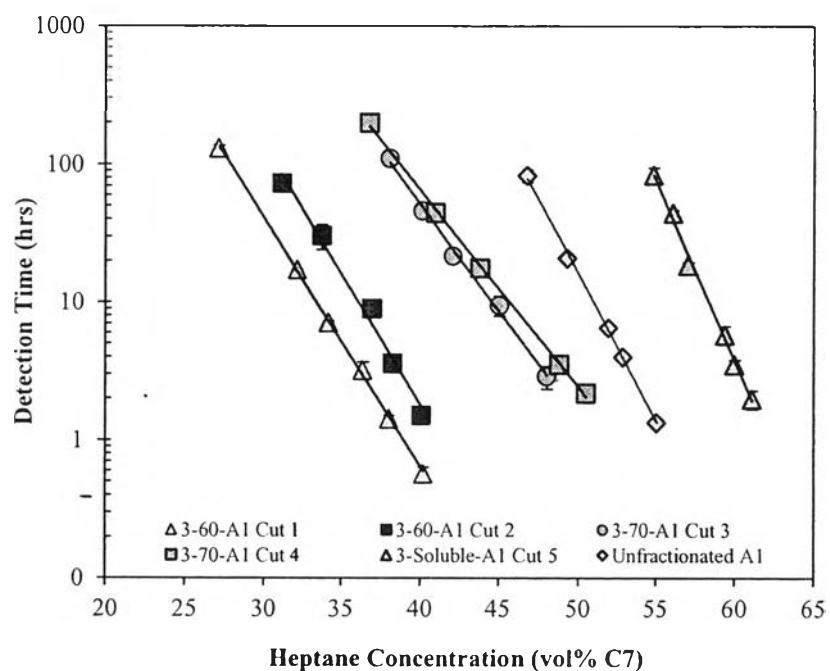
#### 4.2 Microscopy results

The size of nanoaggregates obtained from scattering experiments can imply the stability trends of fractionated asphaltenes. However, scattering technique itself has limitation which can only detect scattering behavior of nanometer length scale particles dispersed in solution. Therefore, microscopy technique, which can be used to observe the time, denoted as detection time, required for destabilized asphaltenes to agglomerate from nano-sized aggregates to micron-sized clusters, was utilized to investigate the precipitation kinetics among asphaltene fractions by an introducing of n-heptane precipitant. Similar to scattering experiments, 1 wt% asphaltene model mixtures were prepared to be performed in microscopy experiments by dissolving all fractionated and unfractionated asphaltenes separately in toluene. Figure 4.3 and 4.4 show the detection time lines of asphaltene fractions separated from 3 wt% A1 and K1 asphaltene solution, respectively. Similar trends of detection line distributions for both types of asphaltenes were observed. Detection lines of Cut 1, which is the fraction that precipitated first and form largest nanoaggregates, locate on the far left of the plot indicating that the asphaltenes precipitated first have the highest tendency

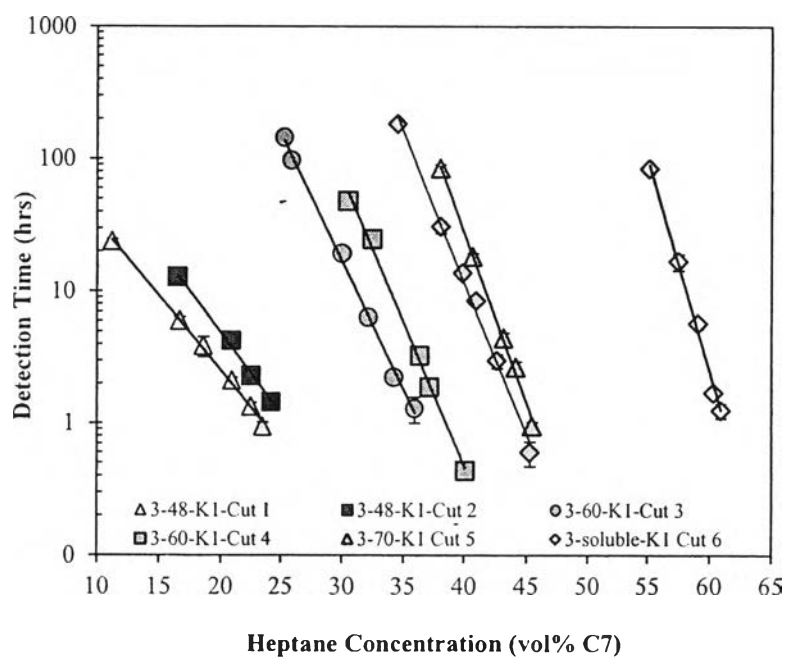
for aggregation and precipitation than the latter precipitated fractions. This finding suggests that first fraction of precipitated asphaltenes, which requires less amount of precipitant to destabilize, is the most unstable fraction. This behavior supports our hypothesis that asphaltenes precipitated first are the most unstable fraction and therefore the most problematic portion of the crude oil. After the most unstable fractions were removed from solutions, asphaltenes remaining in solution became more stable and less polydispersed. The later fractionated asphaltenes precipitated from higher heptane concentrations, the more stable fractions experiencing slower aggregation rates were observed. For the last precipitated fractions of both types of asphaltenes (Cut 5 and Cut 6 for A1 and K1 asphaltenes, respectively), their detection lines locate on the far right of the plot expressing the slowest precipitation kinetics. These fractions consisted of soluble asphaltenes remaining in the supernatant of 70 vol% heptane solution which means that they contain the most stable asphaltenes forming tiniest nanoaggregates. Unfractionated asphaltenes attribute to combination of all fractionated asphaltenes. Their aggregation tendency appear to be slower than that of the last fractions of fractionated asphaltenes, as can be seen that detection lines of unfractionated asphaltenes shifted to the left from last precipitated fractions' lines.

This suggests that performing time and solubility based fractionation can reduce the polydispersed nature of asphaltenes and each fraction of asphaltenes become less polydispersed especially for the last fractions that have higher stability over the unfractionated asphaltenes.

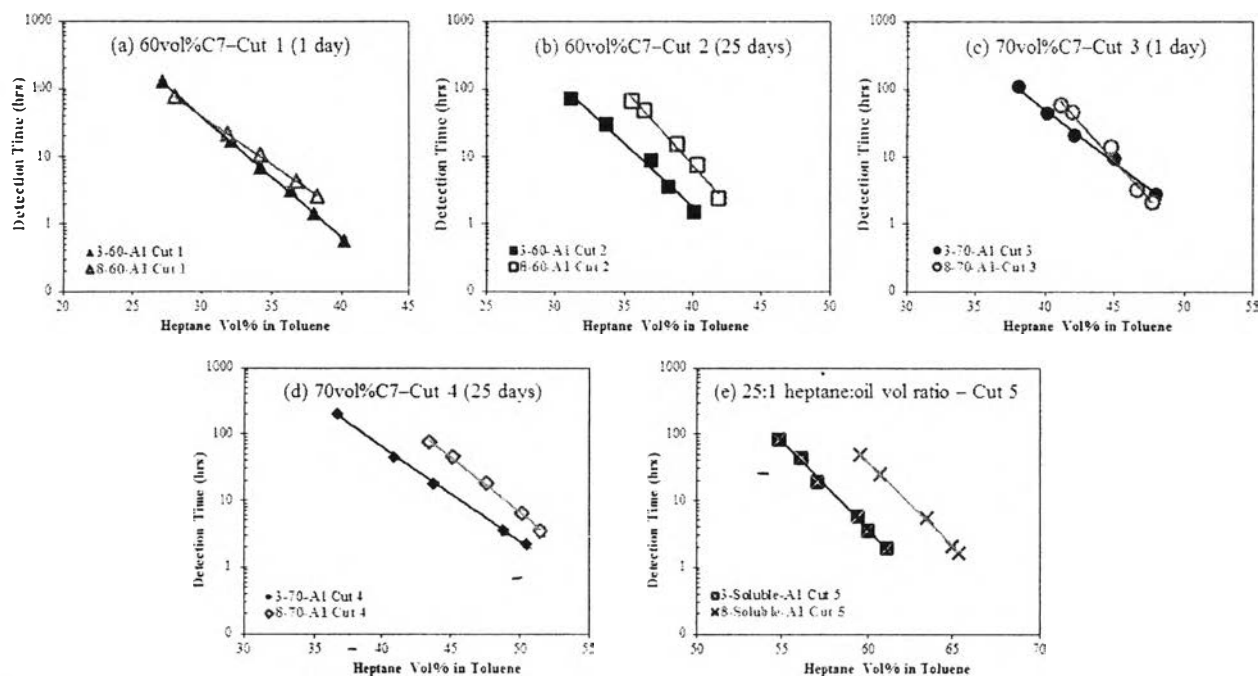
The solubility parameter is a measured number that can express the degree of interaction between materials. In asphaltene system, difference in solubility parameter between asphaltenes and solvent can exhibit the stability of asphaltenes. The smaller difference in solubility parameter of asphaltenes and solution, the more stable asphaltenes dispersed in solvent. Therefore, in this study, measuring solubility parameters of asphaltenes is expected to be a useful tool to characterize the stability among fractionated asphaltenes. Haji-Akbari *et al.* (2013) established the unified model for aggregation of asphaltenes using Schmoluchowski's aggregation equation as shown in equation 4.2. This model can successfully capture the aggregation rates of asphaltenes in different crude oils and solvents.



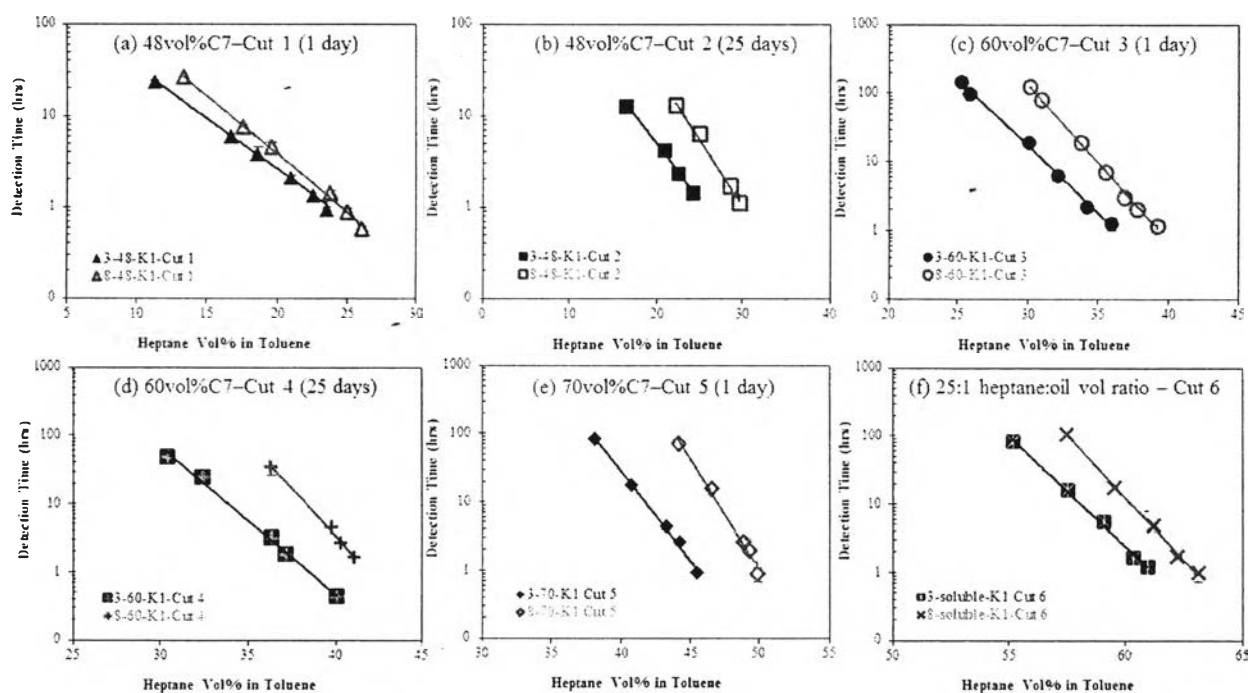
**Figure 4.3** Detection lines of unfractionated A1 asphaltenes and fractionated A1 asphaltenes extracted from 3 wt% asphaltene solution.



**Figure 4.4** Detection lines of unfractionated K1 asphaltenes and fractionated K1 asphaltenes extracted from 3 wt% asphaltene solution.



**Figure 4.5** Detection lines of fractionated A1 asphaltenes extracted from 3 wt% solution (black lines) and 8 wt% solution (blue lines).

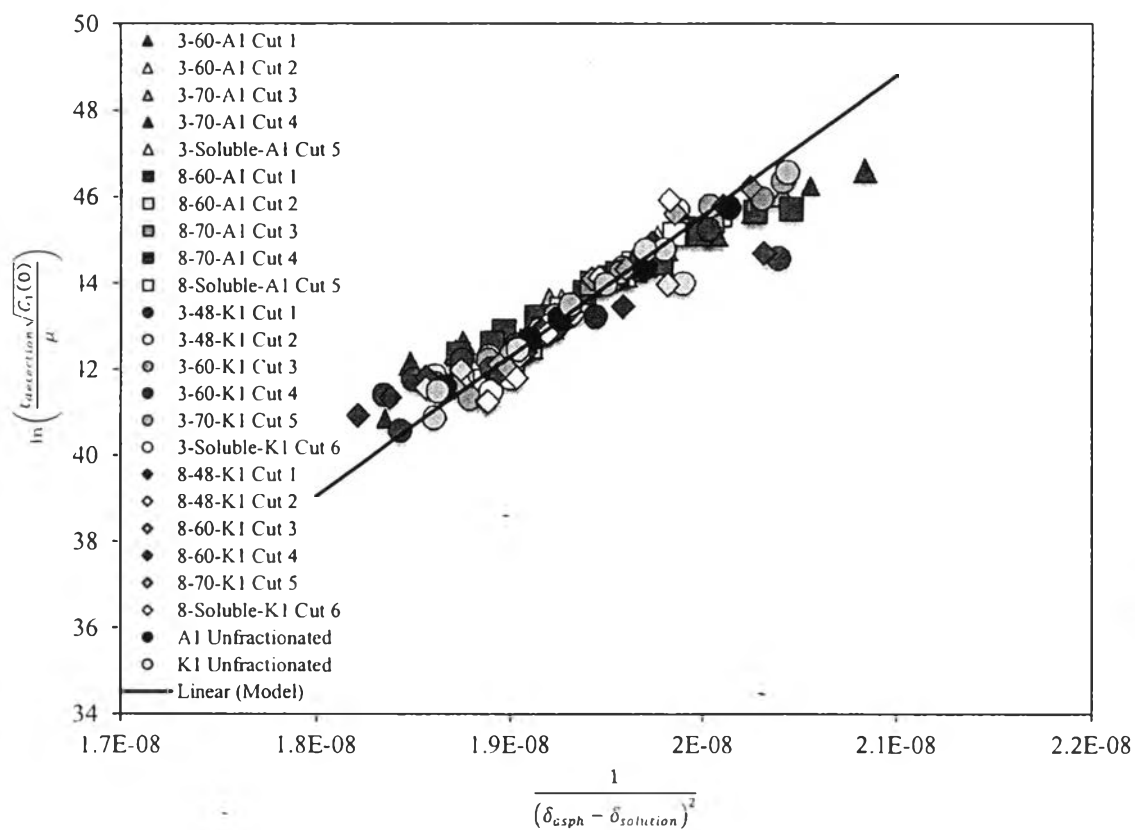


**Figure 4.6** Detection lines of fractionated K1 asphaltenes extracted from 3 wt% solution (black lines) and 8 wt% solution (blue lines).

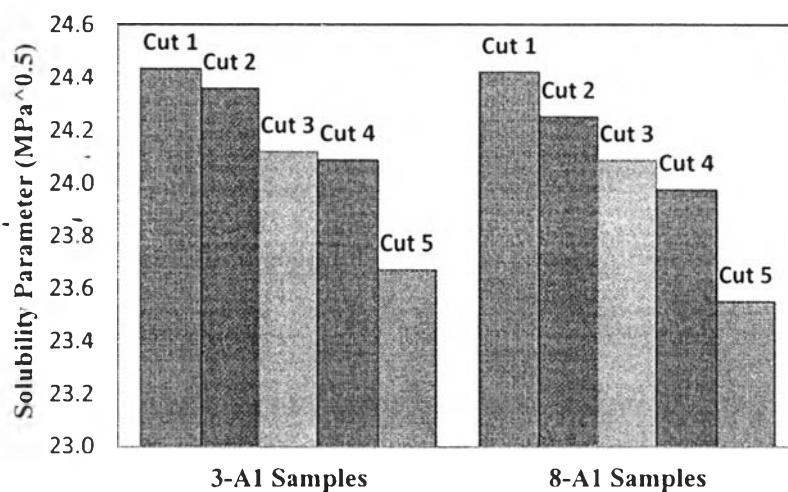


$$\ln\left(\frac{t_{detection}\sqrt{C_1(0)}}{\mu}\right) \propto (\delta_{asph} - \delta_{solution})^n \quad \text{Eq. 4.2}$$

where  $C_1(0)$  is the initial number concentration of aggregating asphaltenes,  $\mu$  is the viscosity of solution and  $\delta_{asph}$  and  $\delta_{solution}$  are the Hildebrand solubility parameter of the asphaltenes and solution, respectively. We used the correlation of the fraction precipitated as a function of  $1/(\delta_{asph} - \delta_{solution})^n$  with  $n=2$  from our effect of asphaltene concentration study to estimate the  $C_1(0)$ . To correlate our previous work and this work together,  $n=2$  in this model was also used in this study. Viscosity and solubility parameter of solutions were calculated using logarithmic averaging and volumetric averaging of individual viscosity and solubility parameter of precipitant and solvent, respectively. The solubility parameter of asphaltenes from different fractions can be estimated by using the master curve of the correlation from the equation 2 with knowing the detection time at fixed precipitant concentration. By applying microscopy data in aggregation model, it can be seen from Figure 4.7 that all data collapsed into single master curves. However, slight deviation from master curves was observed for the fractions which precipitate first at low heptane concentrations (i.e. Cut 1 and Cut 2). As a result of high instability of those unstable fractions, it was observed that microscopy samples, which were destabilized with low heptane concentrations, provide considerable shorter detection times than their times predicted from model causing the deviation from master curve. Figure 4.8 and 4.9 demonstrate the distribution of calculated solubility parameters of fractionated asphaltenes. The results indicating that asphaltenes which precipitated early on time at lower solubility have higher solubility parameters and consequently are more unstable than the fractions precipitate later on time with higher solubility. In addition, all fractions precipitated from higher asphaltene content also have lower solubility than the ones extracted from lower asphaltene content. Therefore, it is shown that the microscopy results along with estimated solubility parameters of asphaltenes from aggregation model are in agreement with the scattering results.



**Figure 4.7** Plot of  $\ln\left(\frac{t_{\text{detection}} \sqrt{C_1(0)}}{\mu}\right)$  vs.  $1/(\delta_{\text{asph}} - \delta_{\text{solution}})^2$  for all fractionated and unfractionated A1 and K1 asphaltenes.



**Figure 4.8** Solubility parameters of fractionated A1 asphaltenes.

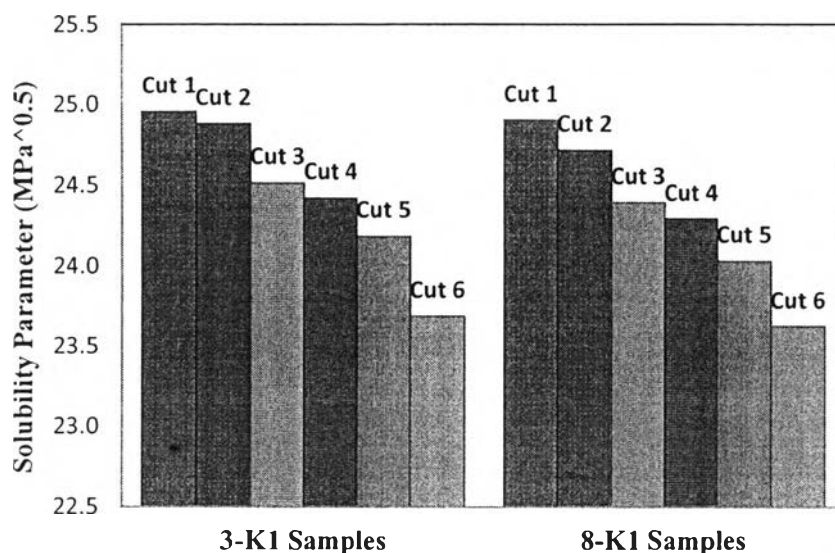
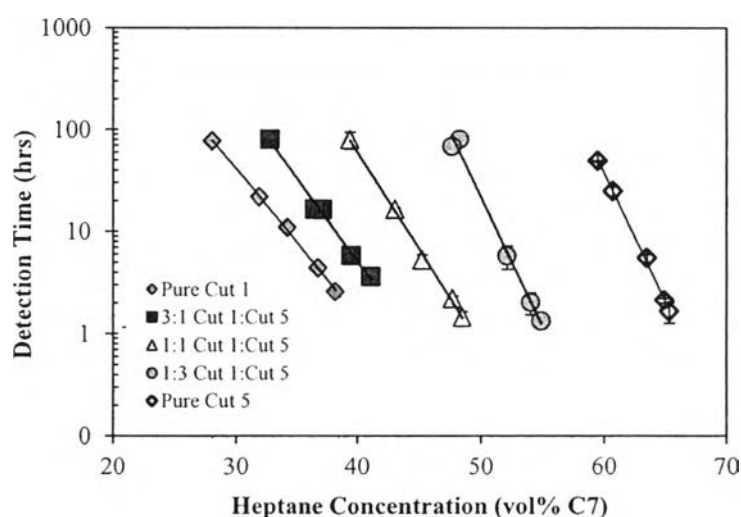


Figure 4.9 Solubility parameters of fractionated K1 asphaltenes.

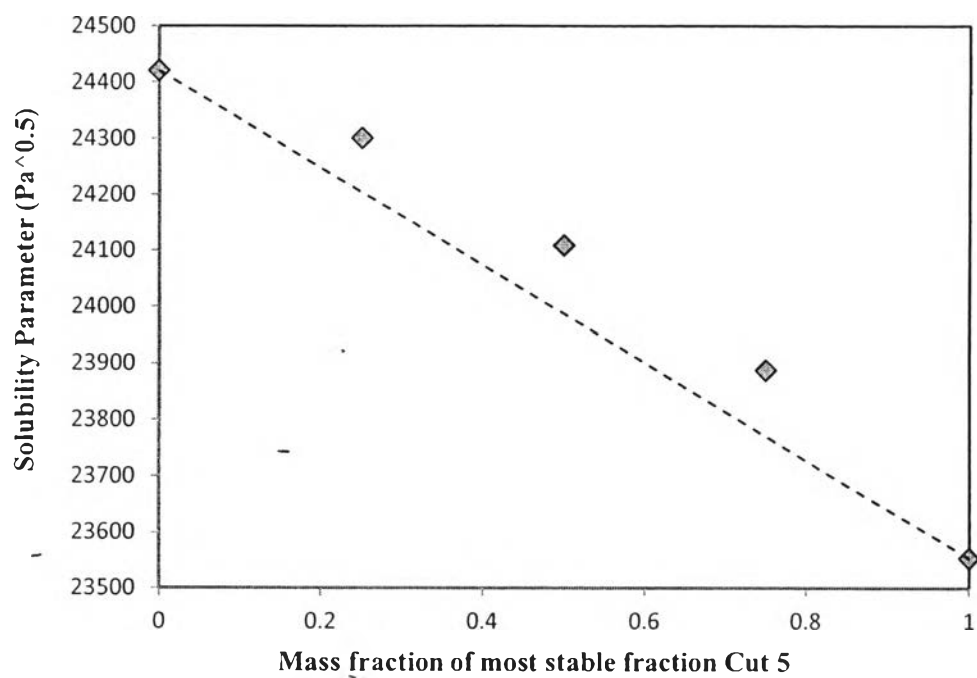
#### 4.3 Mixture of least and most stable asphaltenes

Time and solubility based fractionation were successfully used to diminish complex polydispersed nature of asphaltenes. It was shown that the most unstable asphaltenes are the earliest precipitated fraction from lowest heptane concentration, whereas the most stable asphaltenes are the last fraction precipitated from highest heptane concentration. Least stable asphaltene fraction is also expected to be the most problematic portions in crude oil causing severe deposition problems. In addition, blending of crude oils is normally used in oil production with an aim to reduce the viscosity of oil during transportation. However, change in oil composition by mixing crude oils can cause asphaltenes to be destabilized and precipitated out of solutions. Therefore, it is a great deal to investigate an influence of the blend of most unstable and stable asphaltenes on their aggregation kinetics. Cut 1 and Cut 5 of fractionated A1 asphaltenes from 3 wt% asphaltene solutions, which are the most unstable and stable fractions respectively, were mixed in three different mass ratios: 1:3, 1:1 and 3:1 Cut1 to Cut 5. Those mixtures of asphaltenes were dissolved with toluene separately to obtain 1 wt% blend of asphaltenes model mixtures which were then used to perform in microscopy and scattering experiments. Figure 4.10 shows microscopy results of those three mixtures. It is known that appearance of asphaltenes clusters observed in microscope after destabilization are the most

unstable asphaltenes. It can be seen that the blend containing most fraction of stable asphaltenes has lowest aggregation rate and therefore are the most stable compared to other blends. The aggregation rates of three mixtures can be ordered;  $3:1 > 1:1 > 1:3$  Cut 1 to Cut 5 ratio. The result indicates that more quantity of stable asphaltenes in the mixture of asphaltenes can stabilize the unstable asphaltenes to be more stable and precipitate slower. In addition, estimated radius of gyration of those mixtures are 4.86, 4.50 and 3.29 nm for 3:1, 1:1 and 1:3 Cut 1 to Cut 5, respectively. Scattering results indicate that asphaltenes containing more stable fraction form smaller nanoaggregates leading to be more stable than the mixture containing less stable asphaltenes. Figure 4.11 illustrates solubility parameter of mixed asphaltenes estimated from aggregation model. The dash line shows volumetric average of individual solubility parameters of the least and most stable asphaltenes. It can be observed that even though their solubility parameters decreases as the mass of stable asphaltenes in the mixtures increases, those solubility parameters of mixed asphaltenes are shifted above the volumetric average line. This result suggests that not only the most stable has influence on an increase in stability of the mixtures, but the most unstable asphaltenes also play a role in control their aggregation behavior.



**Figure 4.10** Detection time as a function of heptane concentration of mixtures of A1 least stable (Cut 1) and most stable (Cut 5) fractions extracted from 3 wt% asphaltene solution.



**Figure 4.11** Solubility parameters of mixed Cut 1 and Cut 5 of fractionated A1 asphaltenes at different mass fractions of Cut 5.