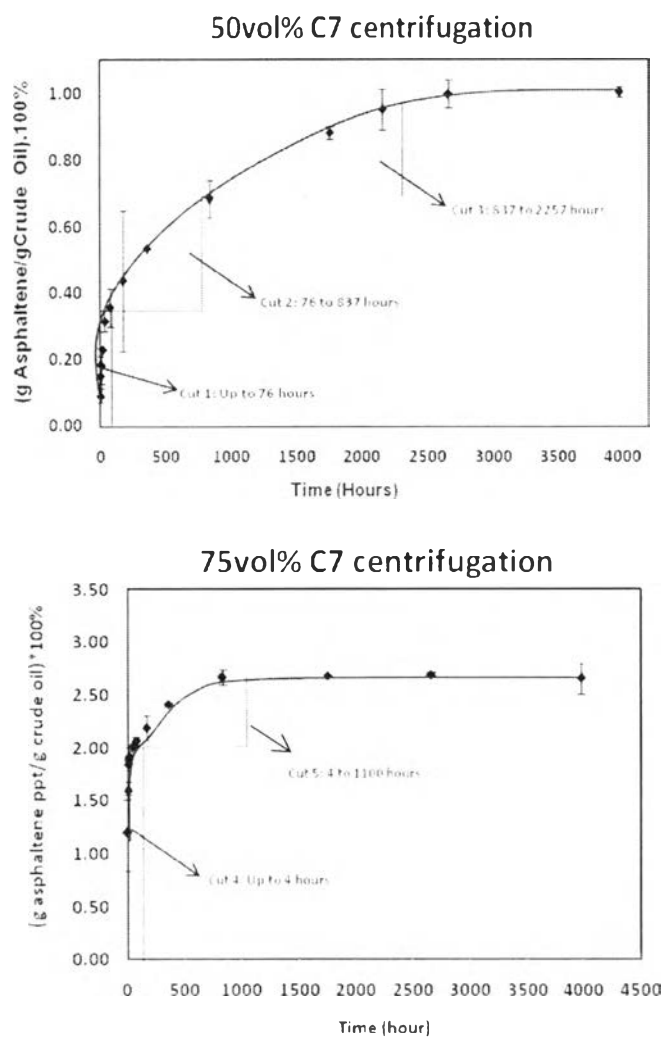


## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Centrifugation and fractionation results

As mentioned in experimental section, fractionation experiments were performed at 50 vol% and 75 vol% of heptane. Figure 4.1.1 shows centrifugation results at 50 vol% (a) and 75 vol% (b).



**Figure 4.1.1** Centrifugation plots at 50 vol% (a) and 75 vol% (b) heptane. The arrows indicated the time steps at which each asphaltene fractions were fractionated.

It is clear from the centrifugation plots that the amount of asphaltenes precipitated increased over time. The fractionation of asphaltene fractions was done according to the time steps indicated by the arrows in Figure 4.1.1. The stability of asphaltene cuts was expected to be in the following order: Cut 1 < Cut 2 < Cut 3 < Cut 4 < Cut 5, suggesting that the fraction that precipitate earlier than the others tends to be more unstable. Each asphaltene fraction (Cut 1 to Cut 5) was then further characterized by various characterization techniques to identify the differences in their properties as a function of time and to further correlate the property differences with their aggregation behavior.

## 4.2 Characterization results

### 4.2.1 Heteroatom and Metal Content results

Amount of heteroatom (C, H, N, O and S), hydrogen per carbon ratio (H/C), and metal content (Ni and V) of asphaltenes were measured by Elemental Analysis and ICP-MS, respectively. Table 4.2.1.1 shows a summary of elemental analysis, H/C ratio and metal content results for each cut.

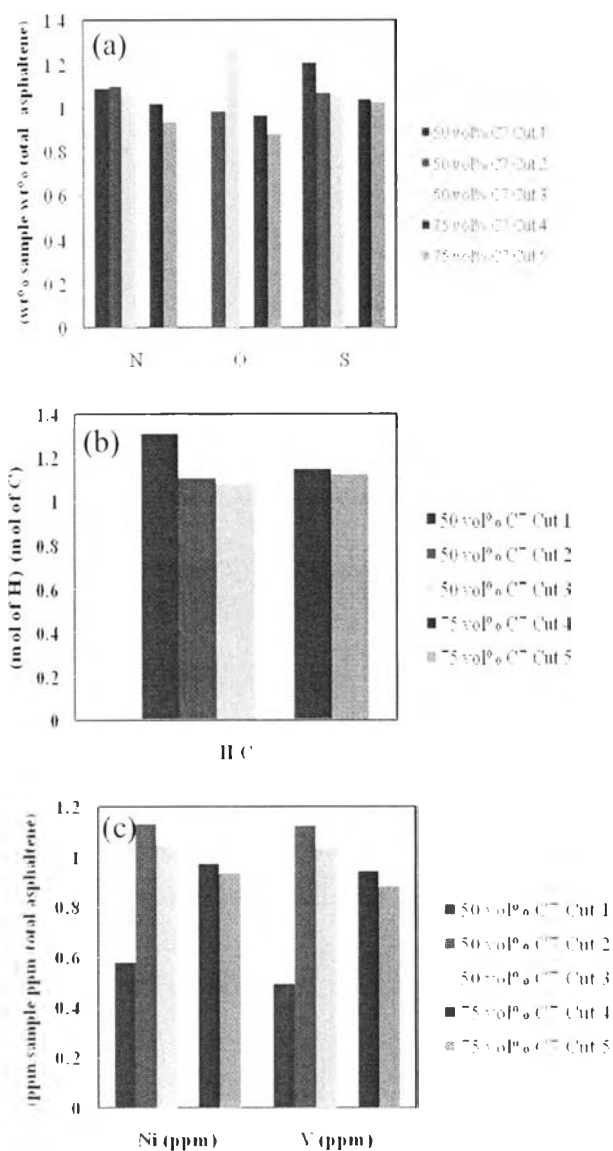
**Table 4.2.1.1** Summary of elemental analysis, H/C ratio and metal content for each cut.

Type of asphaltenes	%wt						Ni (ppm)	V (ppm)
	C	H	N	O	S	H/C		
50 vol% C7 Cut 1	82.86	11.12	0.55	2.7	4.33	1.61	88	237
50 vol% C7 Cut 2	80.9	7.48	1.15	2.17	7.7	1.11	172	537
50 vol% C7 Cut 3	81.41	7.35	1.11	2.79	7.6	1.08	160	495
75 vol% C7 Cut 4	81.27	7.77	1.07	2.13	7.48	1.15	148	453
75 vol% C7 Cut 5	80.61	7.56	0.98	1.94	7.36	1.13	142	424
50 vol% C7 soluble (Cut 6)	81.18	7.81	1.02	1.82	7.26	1.15	139	442
75 vol% C7 soluble (Cut 7)	81.07	7.79	1.01	3.79	7.06	1.15	129	394
Total asphaltenes	81.5	7.79	1.05	2.21	7.2	1.15	152	479

As can be seen from Table 4.2.1.1, H/C ratio of asphaltenes of Cut 1 is approximately 1.6. This value is higher than the average ratio of 1.2 reported for asphaltenes in the literature (Spiecker et al., 2003). It is believed that higher H/C ratio in the first cut is due to wax contamination (H/C ratio of 2 for waxes). During fractionation experiments, crude oils were pretreated by centrifugation at 10,000 rpm for 3 hours to separate any wax or solid

particles. However, due to high viscosity and density of oil which is also close to those of the wax, it is possible that some wax remained in the solution after pretreatment. By adding 40 vol% of heptanes, the remaining wax should be centrifuged.

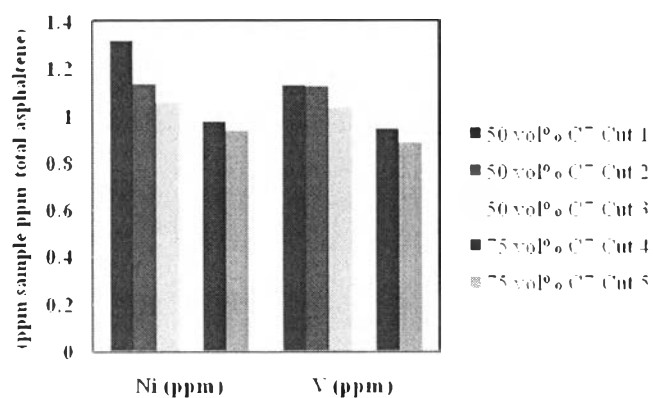
Figures 4.2.1.1(a), (b) and (c) illustrate clear comparisons of heteroatoms, H/C ratio and metal contents in different asphaltene cuts, respectively. It is to be noted that all the experimental data were normalized by the total asphaltene values except for H/C ratio data. From the results, it can clearly be seen that there was no significant difference in the trend for the heteroatom content except for nitrogen and sulfur (excluding Cut 1). The metal content results showed a very clear decreasing trend from the first precipitated fraction to the last precipitated fraction (excluding Cut 1). A proposed explanation for this behavior could be due to the contamination of wax in our Cut 1. It is also interesting to consider how nitrogen and sulfur are only present within the aromatic cores and they are the two elements that show trends in the elemental analysis results. The positions and associations of these elements within the aromatic cores of the asphaltenes molecules could also influence the results.



**Figure 4.2.1.1** Elemental composition of (a) heteroatoms, (b) H/C ratio and (c) metal contents for different asphaltene cuts.

Due to wax contamination in Cut 1, an assumption was made to estimate the actual metal content of Cut 1 asphaltenes by eliminating the effect of wax. Figure 4.2.1.1(b) shows that H/C ratio is relatively constant for all of the cuts except Cut 1. However, it has a higher value in Cut 1 due to wax contamination. An average of the H/C ratios for the other cuts was taken and assumed that the same ratio is valid for Cut 1 asphaltenes. By knowing the actual H/C ratio, the fraction of wax contaminated in the first cut asphaltenes was estimated. Waxes do not contain metal in their structures,

therefore by knowing the wax fraction in Cut 1, the metal content of the asphaltenes could also be estimated. It was found that actual amount of nickel and vanadium for Cut 1 is the largest compared to other cuts. Higher metal content of asphaltenes in first cut results in higher polarity and stronger tendency to aggregate and consequently faster precipitation. The estimated metal contents for Cut 1 compared to other cuts are shown in Figure 4.2.1.2.



**Figure 4.2.1.2** Metal contents for different asphaltene cuts (without wax).

To overcome the wax problem, the experimental procedure was modified to generate pure Cut 1. In the modified procedure, pretreated oil was diluted with 40 vol% heptane to reduce the density and viscosity enhancing better wax separation. According to the microscopy results, no asphaltenes were expected to precipitate within 24 hours at 40 vol% heptane concentration. The waxes were then centrifuged 1 hour after heptane addition and more heptane was added to the solution to reach to 50 vol% and generate first cut with no wax (new experimental procedure outlined in experimental section). Table 4.2.1.2 shows the elemental composition for the new Cut 1. The H/C has reduced from 1.6 to 1.3 supporting that most of the wax is separated. However, 1.3 is still larger than expected value for asphaltenes so there might still be some wax contamination in new Cut 1.

**Table 4.2.1.2** Elemental composition and H/C ratio of new Cut 1.

Type of asphaltenes	C wt%	H wt%	N wt%	O wt%	S wt%	Atomic H/C	Atomic O/C
50% C7 new Cut 1	82.26	8.99	0.89	-	6.75	1.3129103	-
	82.17	9.27	0.63	-	6.38	1.3581599	-

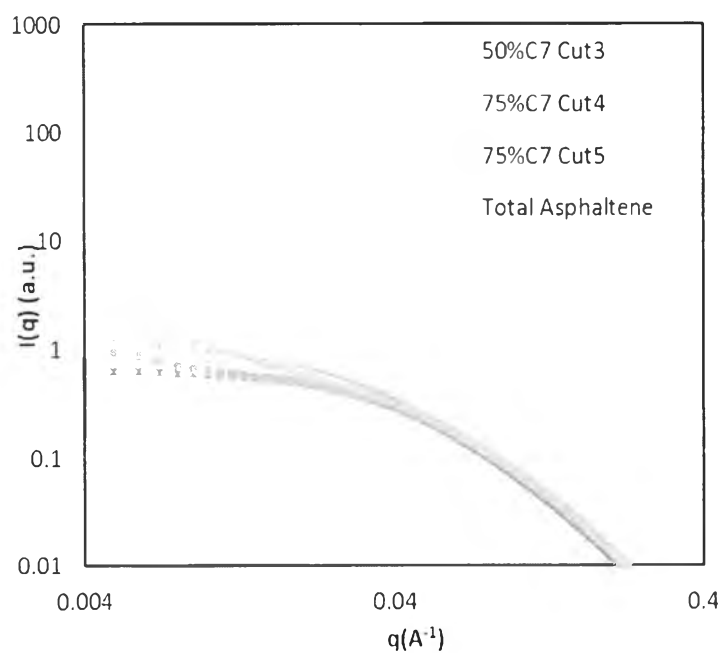
#### 4.2.2 Size of nanoaggregate results

Prior to performing scattering experiments, fractions of asphaltenes were dissolved in toluene. It was found that a small fraction of new Cut 1 was insoluble in toluene. Table 4.2.2.1 shows the fraction of new Cut 1 soluble and insoluble in toluene. The insoluble fraction was centrifuged before scattering experiments were conducted.

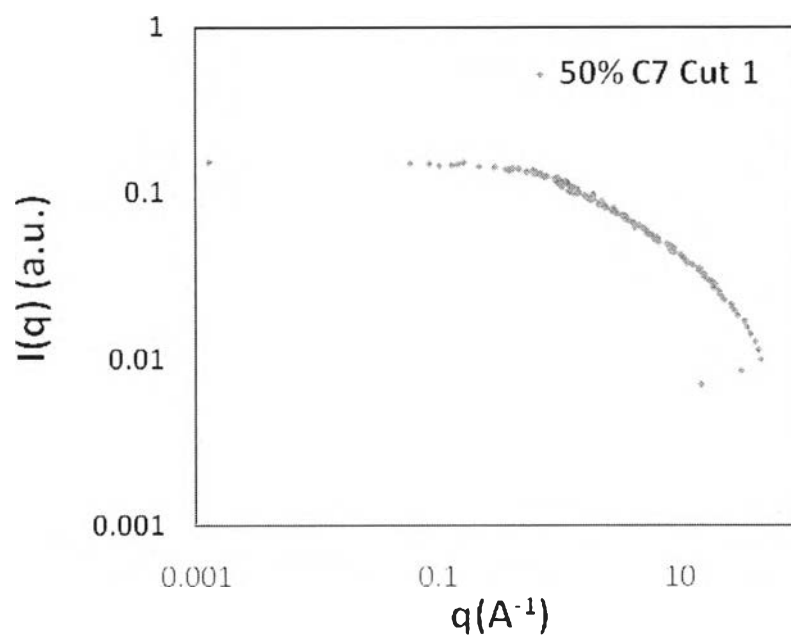
**Table 4.2.2.1** Soluble and insoluble fractions of new Cut 1.

Type of asphaltene	Soluble fraction (in toluene)	Insoluble fraction (in toluene)
50 vol% C7 Cut 1	91.71%	8.29%

The scattering profiles for different cuts are shown in Figure 4.2.2.1 and Figure 4.2.2.2. The scattering profile shown in Figure 4.2.2.1 was performed at the Argonne National Laboratory and the scattering profile shown in Figure 4.2.2.2 was performed at the University of Michigan.



**Figure 4.2.2.1** Scattering profiles for different cuts of asphaltene performed at Argonne National Laboratory.



**Figure 4.2.2.2** Scattering profile for new Cut 1 performed at the University of Michigan.

Cut 1 generated by modified experimental procedure gave the largest size of nano-aggregates compared to the other cuts. The results suggest that

asphaltenes that precipitate first form larger nanoaggregates in the solution, are the most unstable fraction and has larger aggregation tendency. Table 4.2.2.2 shows the comparison of radius of gyration for different cuts.

**Table 4.2.2.2** Radius of gyration for different asphaltene cuts.

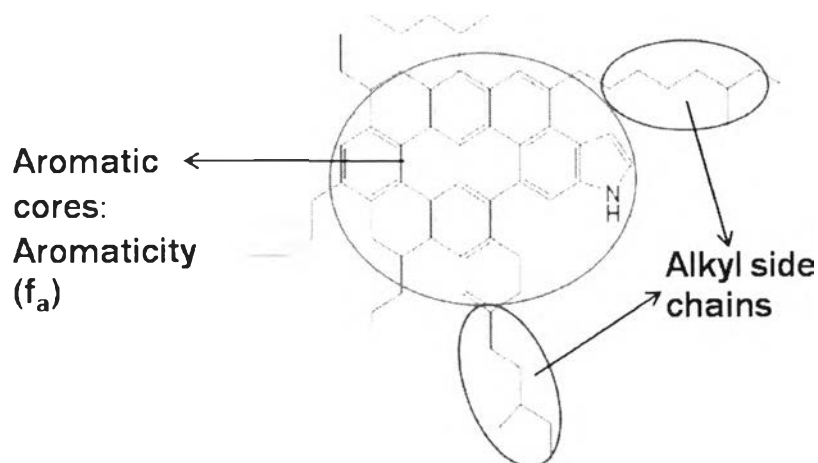
Concentration	$R_g^*$ (nm)	
50 vol% C7	Cut 1 (new)	$7.39 \pm 0.34$
	Cut 3	$5.15 \pm 0.15$
75 vol% C7	Cut 4	$3.79 \pm 0.07$
	Cut 5	$3.70 \pm 0.06$

\*The radius of gyration for each cut was obtained from fitting the scattering profiles to the Guinier Approximation (Equation 3).

### 4.2.3 Aromaticity and Average alkyl side chain lengths results

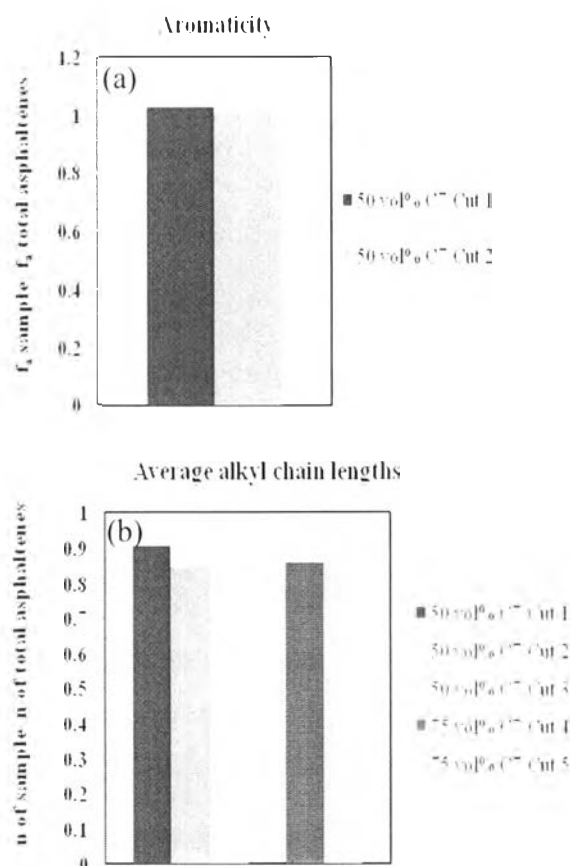
To investigate further whether or not asphaltenes precipitated at different times are just different in physical sizes or they are also different in chemical structure, proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) Nuclear Magnetic Resonance (NMR) were performed to measure the average alkyl side chain length and aromaticity of asphaltene cuts. Figure 4.2.3.1 shows the diagram of a hypothetical asphaltene molecule with the aromatic cores and the alkyl side chains.





**Figure 4.2.3.1** Hypothetical asphaltene molecules with aromatic cores and alkyl side chains (Mullins, 2010).

In general, the aromaticity provides an estimate about the attraction tendency between the aromatic cores. If an asphaltene molecule has a large aromatic core, it indicates that the molecule has strong attraction forces and will be able to aggregate with a neighboring molecule easily. It is also believed that asphaltenes are sterically stabilized by the alkyl side chains surrounding the aromatic cores. Hence, the average alkyl side chain length gives an estimate about the strength of steric repulsion forces between asphaltene particles. The magnitudes of attraction and repulsion forces dictate the stability or aggregation tendency of asphaltenes. Therefore, if an asphaltene molecule has short alkyl side chain lengths, it will have low steric repulsion force which increases the chances of asphaltene molecules to move closer and aggregate with each other resulting in precipitation.



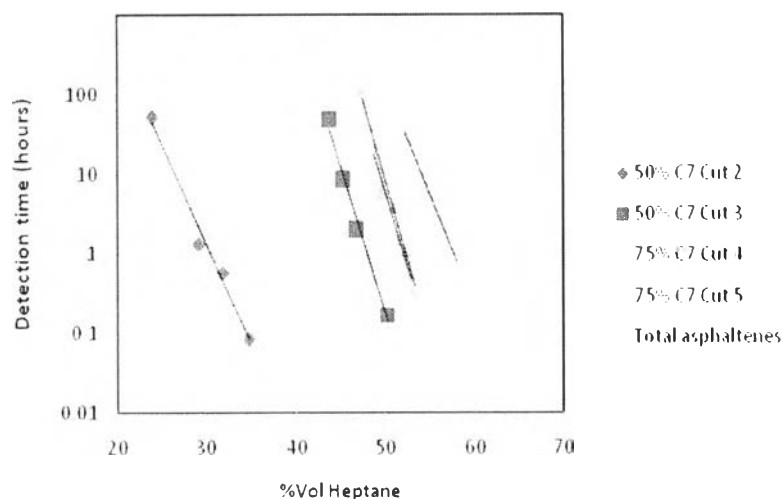
**Figure 4.2.3.2** Aromaticity (a) and average alkyl side chain lengths (b) of different asphaltene cuts.

From Figure 4.2.3.2 (a), it can be seen that the aromaticity of new Cut 1 is slightly higher than Cut 2. The aromaticity of Cut 3, 4 and 5 were not reported because there were not enough dry asphaltene fractions to perform the experiments. As can be seen in Figure 4.2.3.2 (b), the average alkyl side chain lengths for new Cut 1 is highest which is opposite of the expected trend. A possible explanation could be due to the fact that when dissolving new Cut 1 in deuterated methylene chloride, the insoluble fraction of new Cut 1 could not entirely dissolve in this solvent and therefore, the  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra obtained were not the representative spectra of the real "first cut". Also, due to some contamination of wax in new Cut 1, the value of the average alkyl side chain lengths could be influenced by the effect of wax particles. To better understand the results of the average alkyl side chain length, it is also interesting to consider the asphaltene structure. As it is well

accepted that there are two types of asphaltene structure, archipelago and island model, it is assumed that asphaltene molecules studied here have the island model which might not necessarily be the case. As mentioned earlier that aromaticity provides an estimate about the attraction tendency between the aromatic cores, hence, if the aromaticity is high, it is implied that there would be larger aggregation tendency and consequently precipitation. New Cut 1 is expected to have highest aromaticity since it is the first fraction to precipitate; however, as shown in Figure 4.2.3.2 (a), new Cut 1 has relatively the same aromaticity as compared to Cut 2 indicating that new Cut 1 and Cut 2 are not highly structurally different. This claim is also supported by the average alkyl side chain lengths measured from  $^1\text{H}$  NMR. Therefore, although new Cut 1 seems to be the most unstable fraction because it is the first fraction to precipitate, the differences in asphaltene properties observed from NMR were not significant.

#### **4.3 Microscopy results**

The aggregation rate of asphaltene is controlled by the interaction between the particles, therefore, if the interactions are different then definitely the aggregation rate will be different. However, after investigating the properties of asphaltene cuts precipitate at different times, it was found that the properties were not significantly different. This result leads to another interesting aspect of asphaltene precipitate behavior. Since the properties of the asphaltene fractions were very similar, it was expected that their aggregation rate would also be similar. Microscopy experiments were performed to test this hypothesis. It was found that the aggregation behaviors of the asphaltene that precipitate at different times are significantly different as can be seen from Figure 4.3.1.



**Figure 4.3.1** Detection time vs. %vol heptane for different asphaltene cuts.

The detection time plot showed that the fraction that precipitates earlier (Cut 2) has significantly higher aggregation rate than the fraction that precipitate later indicating that the first fraction that precipitate out of the solution is the most unstable fraction and it requires less amount of precipitate to destabilize it. It can also be observed that the onset profiles for 75 vol% Cut 4 and Cut 5 superimpose each other. This suggests that at higher precipitant concentration, the fraction of asphaltenes that precipitate out of the solution is the very stable since it requires more heptanes to destabilize it but the influence of the precipitant concentration on the aggregation rate is minimal. The onset profile of the total asphaltene lies on the far right of the plot because in order to precipitate total asphaltene, it requires a 40:1 volume ratio of heptane : crude oil which is equivalent to 95-97 vol% heptane. Therefore, total asphaltene is the fraction that is the most stable fraction. The fact that the onset profile of each cut is different signifies that there is a difference in the aggregation behavior of asphaltene precipitated at different times. However, due to the highly polydispersed nature of asphaltenes, it is still unclear whether what properties could be causing this difference. In the work of Haji Akbari Balou et al., 2012, it discussed about a unified model for aggregation of asphaltene. In this work, it incorporated the use of the model to better explain the aggregation behavior of asphaltenes. By applying the model, the solubility parameter of asphaltene fractions

can be calculated. It was found that there is a solubility distribution among the asphaltene fractions and that the fraction that precipitate earlier than the other has higher solubility parameter. Table 4.3.1 shows the solubility parameter of each asphaltene cut.

**Table 4.3.1** Solubility of each asphaltene cuts.

Asphaltene fractions	Solubility parameter ( $\text{Pa}^{1/2}$ )
50 vol% C7 Cut 2	24590
50 vol% C7 Cut 3	24030
75 vol% C7 Cut 4	23860
75 vol% C7 Cut 5	23900
Total Asphaltenes	23750

The solubility distribution among the asphaltene fractions precipitated at different times might be an indication why they have different aggregation rate. It would also be interesting to investigate the collision efficiency distribution among the asphaltene fractions and could be done as a future work for this project.