

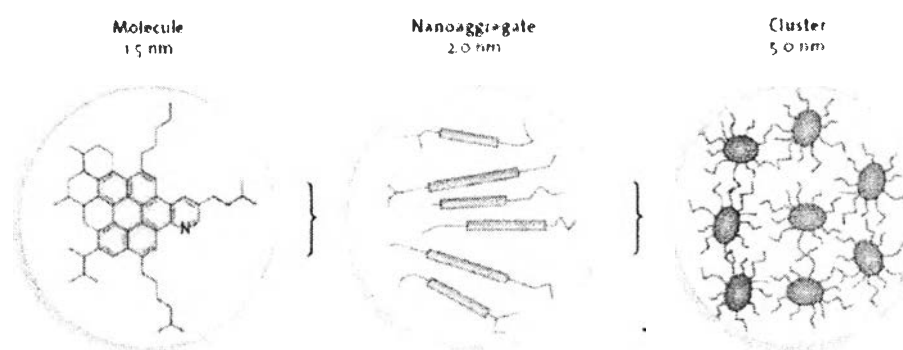
## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Asphaltenes

Petroleum crude oil is a mixture of diverse molecules with different chemical and physical properties and is usually fractionated into four major categories: asphaltenes, resins, small ring aromatics, and saturates (Wattana, 2004). Asphaltenes are the heaviest and most polarizable fraction of the crude oil and are defined functionally as fraction of crude oil soluble in aromatic solvents such as toluene and insoluble in normal alkanes such as heptane (Permsukarome *et al.*, 1997). They are composed of condensed polynuclear aromatic rings, traces of heteroatoms (S, N, and O) and small amounts of metal content such as nickel and vanadium (Ancheyta *et al.*, 2002). According to complex nature of asphaltenes, the chemical structure of asphaltenes has still been difficult to identify. However, the well-known island model has been proposed to describe the architecture of asphaltenes since several decades ago. This proposed model illustrates that each asphaltene molecule is composed of only one or two fused polycyclic aromatic hydrocarbons (PAHs) surrounded by peripheral alkyl chains (Dickie *et al.*, 1967). Extensive works has modified the island model to be widely accepted model in asphaltene sciences which is “Yen-Mullin model”. As can be seen in Figure 2.1.1, this model showed that moderated-sized polycyclic aromatic hydrocarbon ring system can form asphaltene nanoaggregates with estimated aggregation number of 6 and consequently form clusters of nanoaggregates with aggregation number around 8 (Mullins, 2010).

Asphaltenes are believed to exist as aggregated colloidal particles in the crude oils (Betancourt *et al.*, 2008) and model mixtures (Andreatta *et al.*, 2005). Changes in composition, pressure or temperature during oil production can cause destabilization of colloidal asphaltenes (Mullins *et al.*, 2012). Once destabilized, asphaltenes tend to aggregate into clusters and deposit. Their deposition can lead to plugging of reservoir wells and pipelines causing the reduction in oil production capacity (Hoepfner *et al.*, 2013).



**Figure 2.1** Yen-Mullins model (Mullins *et al.*, 2012).

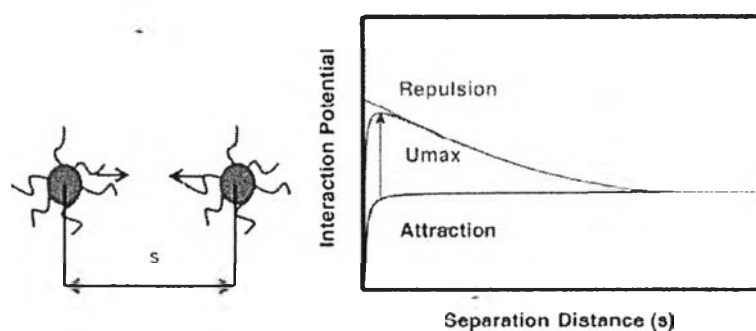
## 2.2 Asphaltene Precipitation

Destabilization and precipitation of asphaltenes are usually induced by adding precipitant into crude oils or model mixtures. As mentioned earlier, asphaltenes can be destabilized and tend to aggregate forming micron-sized clusters and sequentially precipitate out of solution as a result of changes in temperature, pressure or composition. Several molecular interactions, such as London dispersions, acid/base interactions, coordination complex of metals, hydrogen bonding, association of apolar and alkyl groups in hydrophobic pockets, and aromatic pi-pi stacking have been proposed to cause the aggregation of asphaltenes (Karimi *et al.*, 2011). However, it is believed that the most dominant interaction between asphaltenes during aggregation process is the London dispersion force (Haji-Akbari *et al.*, 2013).

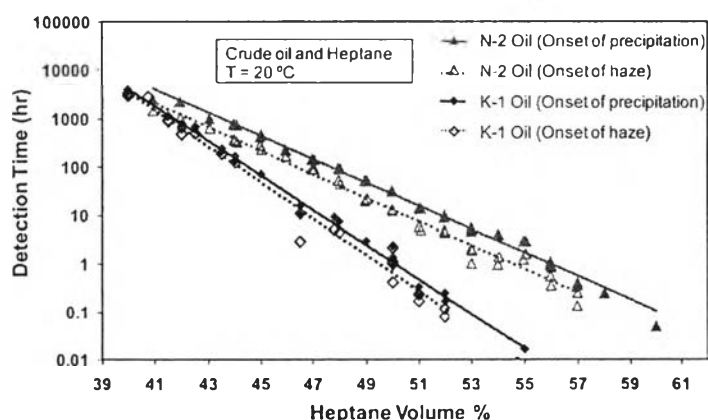
Haji Akbari *et al.* (2013) mentioned that the strength of interaction forces between aggregating asphaltenes are the controlling factor of aggregation tendency of asphaltenes. As shown in Figure 2.1, they described that the success of attachment between two colliding asphaltene particles requires two major conditions: attractive forces must be larger than repulsive forces, and each particle has to have enough thermal energy during collision to overcome the repulsive barrier.

For decades, it was believed that asphaltenes precipitation is a solubility-driven process (Maqbool *et al.*, 2009). Therefore it was assumed that below a critical precipitant concentration, onset volume fraction, asphaltenes remain stable in the solution. However, Maqbool *et al.* (2009) showed that precipitation of asphaltenes is

a kinetically driven process especially at low precipitant concentrations. He studied the kinetics of asphaltene precipitation from two different crude oils using n-heptane as a precipitant. By using optical microscopy, they recorded the time that it took for asphaltenes to become detectable after precipitant addition at different heptane concentrations. Their findings revealed that at high heptane concentrations, the time required to detect asphaltene instability was shorter than the solutions with lower heptane concentration. As can be seen in Figure 2.2, the detection time increased exponentially with decreasing heptane concentration. Thus, there is no single precipitant concentration which can be defined as the critical precipitant concentration.

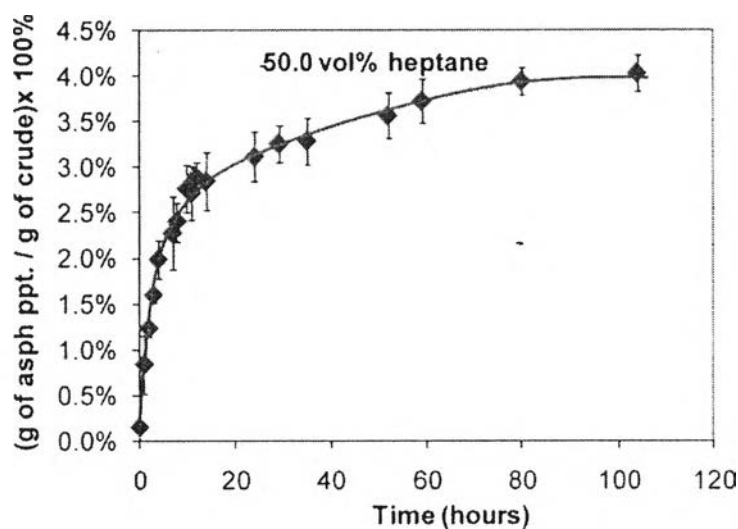


**Figure 2.2** Schematic of interaction between two colliding asphaltene particles (Haji-Akbari *et al.*, 2013).



**Figure 2.3** Detection times for onset of precipitation and onset of haze for varying heptane concentrations using K-1 and K-2 crude oils (Maqbool *et al.*, 2009).

Maqbool et al. also quantified the amount of precipitated asphaltenes as a function of time. Figure 2.4 shows the amount of precipitated asphaltenes gradually increases with time and eventually reaches the plateau. This finding indicates that asphaltenes which precipitated at different times might have differences in properties, and the fraction the precipitated earlier are expected to be more unstable than latter precipitated fractions.



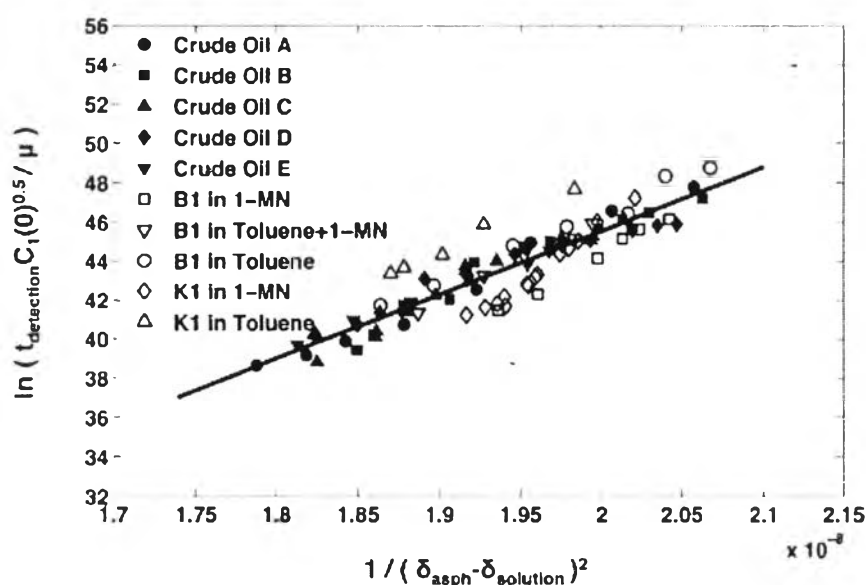
**Figure 2.4** Centrifugation result of asphaltenes precipitated at 50 vol% heptane (Maqbool *et al.*, 2009).

### 2.3 A Unified Model for Aggregation of Asphaltenes

The model of asphaltene aggregation has been developed with an aim to investigate properties controlling asphaltene precipitation kinetics (Haji-Akbari *et al.*, 2013). Their work elucidated that properties of crude oils and solvents used to destabilize asphaltenes in model mixtures play an important role in controlling aggregation rates of asphaltenes as a result of changes in viscosity and solubility parameter of solution.

$$\ln\left(\frac{t_{\text{detection}}\sqrt{C_1(0)}}{\mu}\right) \propto (\delta_{\text{asph}} - \delta_{\text{solution}})^2 \quad \text{Eq. 2.1}$$

This model, as shown in equation 2.1, consolidated the asphaltene precipitation detection time with the difference between solubility parameter of asphaltenes and solution square. It has successfully capture the kinetics of asphaltenes precipitation of ten different crude oils and model mixtures as can be seen from Figure 2.5 that all experimental data collapsed on single master curve developed by their study.



**Figure 2.5** Single master curve of unified model for aggregation of asphaltenes (Haji-Akbari *et al.*, 2013).

Solubility parameter of asphaltenes which is the fitting parameter of the correlation in equation 2.1 can be estimated by knowing detection time of precipitation ( $t$ ), viscosity of solution ( $\mu$ ), solubility parameter of solution ( $\delta_{solution}$ ), and initial number of asphaltene particles  $C_1(0)^{0.5}$ .

## 2.4 Asphaltene Characterization

As mentioned in previous section regarding asphaltene precipitation, numerous studies have been therefore trying to understand destabilization and precipitation mechanism of asphaltenes using various characterization techniques to

identify the most unstable asphaltenes which are expected to be the most problematic fractions (Calemma *et al.*, 1995, León *et al.*, 1999, Ancheyta *et al.*, 2002, Hoepfner *et al.*, 2013) For example, Calemma *et al.* (1995) used  $^{13}\text{C}$  NMR to characterize asphaltenes extracted from seven crude oils by adding excess heptane at 40:1 volume ratio of heptane to oil. They observed the significant trends in molecular structure of asphaltenes as a function of carbon content. They concluded that high carbon content asphaltenes have high aromaticity and aromatic core size, but have low average alkyl chain lengths and heteroatom content.

Leon *et al.* (1999) investigated the correlation between stability and chemical structures of asphaltenes from four crude oils which were classified into two types: stable and unstable crude oils. They found that asphaltenes from unstable crude oils contain lower hydrogen to carbon ratio and have higher aromaticity compared to the ones from stable crude oils.

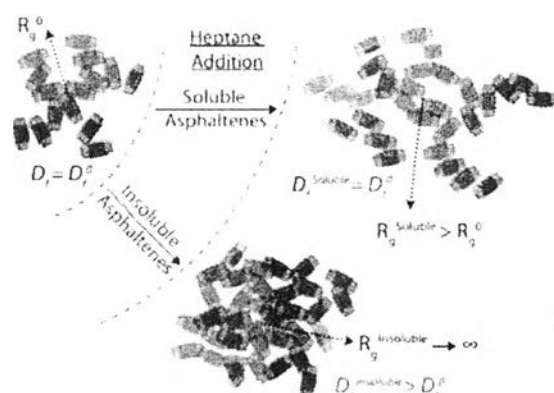
Ancheyta *et al.* (2002) extracted four precipitated asphaltenes from three different crude oils (Maya, Isthmus and Olmeca) by adding two precipitants (n-pentane and n-heptane). The precipitated asphaltenes were then characterized by using VPO molecular weight, liquid state  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and elemental analysis. Their results indicated that precipitant type plays an important role in the composition of precipitated asphaltenes; asphaltene precipitated from n-heptane have higher molecular weight and aromaticity than n-pentane asphaltenes.

Hoepfner *et al.* (2013) used small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) techniques to study asphaltene structure and stability in crude oils and model systems, Their findings showed that asphaltenes have a fractal structure. Soluble asphaltenes were found as fractal clusters having the fractal dimension which is independent upon heptane concentration. Nevertheless, once asphaltenes were destabilized, insoluble asphaltene clusters have higher fractal dimension compared to the soluble ones. The schematic of their experimental findings is shown in Figure 2.6, where  $R_g^0$  and  $D_f^0$  represent the radius of gyration and fractal dimension, respectively. Their results also revealed that as a result of the packing arrangement of asphaltene nanoaggregates, the modification of structure of fractal clusters is therefore occurred simultaneously.

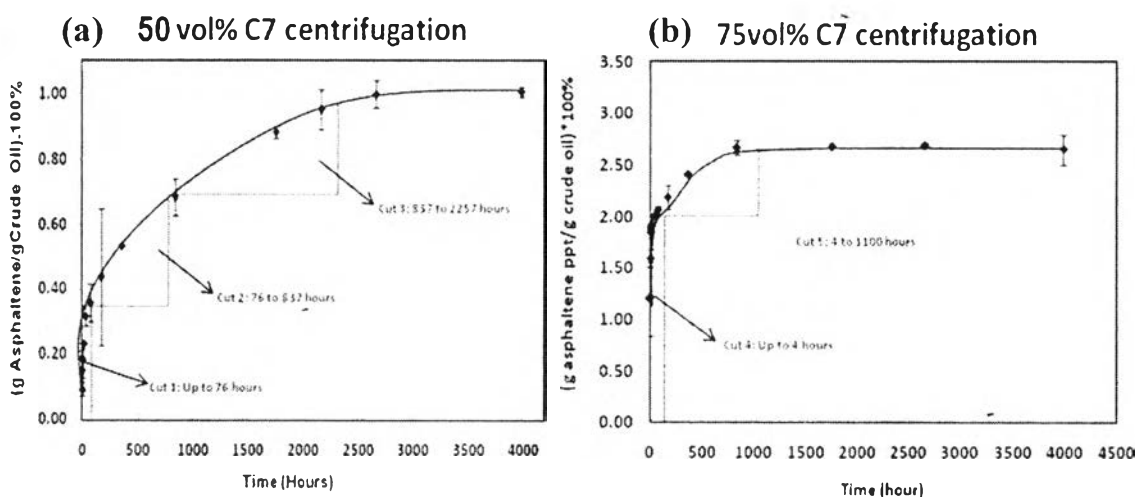
Extensive studies have attempted to fractionate asphaltenes into subfractions based on their solubility aiming to better understand the polydispersed nature of asphaltenes (Buenrostro-Gonzalez *et al.*, 2002, Wattana, 2004). For instance, Buenrostro-Gonzalez *et al.* (2002) used proton nuclear magnetic resonance ( $^1\text{H}$  NMR) to determine the aromaticity of Maya asphaltenes suspended in toluene which were then sequentially fractionated by solubility in acetone and n-heptane. Their results showed that the most stable asphaltenes have smallest aromaticity. Wattana (2004) investigated the differences in properties of asphaltenes precipitated from different sources (crude oils and field deposits) by using polarity based fractionation at different precipitant concentrations. She found significant difference in the distribution of the polar fractions among the asphaltenes extracted from different sources. The field deposits, which were expected to contain the most unstable asphaltenes, distributed the highest portion of the polar fraction. The results from dielectric constant measurements indicated that field deposit asphaltenes have higher tendency to aggregate in toluene at very low concentration compared to asphaltenes fractionated from crude oils. Her finding suggested that asphaltenes which have higher polarity are more unstable than the lesser polar asphaltenes.

To investigate the effect of time on precipitated asphaltenes, Maqbool *et al.* (2009) had attempted to characterize GM2 asphaltenes precipitated at different times. They fractionated asphaltenes at three different times and precipitant concentrations. The properties of precipitated fractions were investigated by measuring dielectric constant and metal contents. Results from this work showed fraction precipitated at lowest precipitant concentration has higher dielectric constant and metal content compared to fraction precipitated at the highest heptane concentration. However, the differences were not significant enough to draw any conclusions about differences in properties precipitated at different times.

Extensive study from Maqbool's work (Masirisuk, 2012, Somkhan, 2013) continued to perform fractionation of A1 asphaltenes as a function of time at two different heptane concentrations. They generated five asphaltene fractions, called "cuts", at different times (three cuts for 50 vol% heptane and two cuts for 70 vol% heptane), as illustrated in Figure 2.7.



**Figure 2.6** Schematic of proposed the modification of fractal dimension of asphaltene precipitation mechanism (Hoepfner *et al.*, 2013).



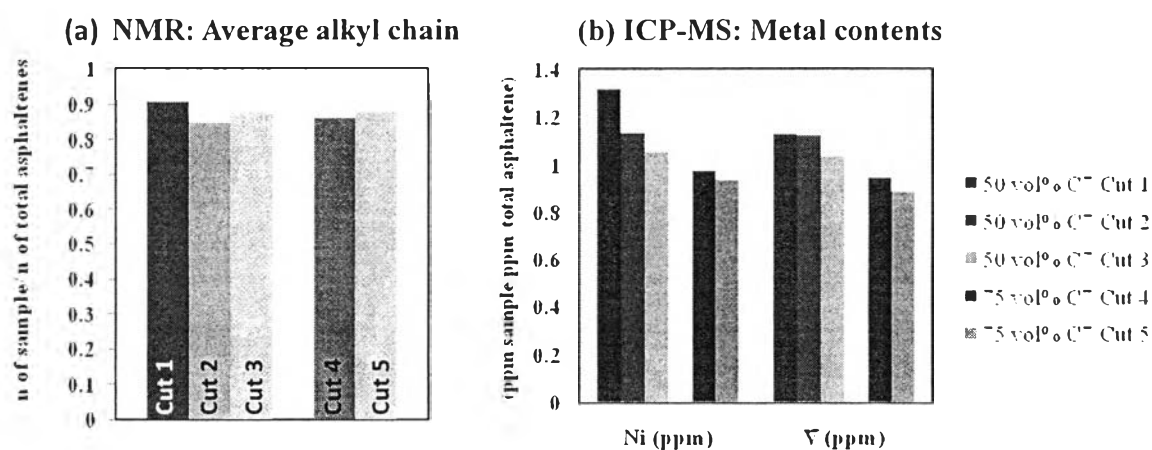
**Figure 2.7** Centrifugation plots at (a) 50 vol% heptane and (b) 75 vol% heptane (Masirisuk, 2012).

The asphaltenes from each cuts were characterized using various techniques such as small angle x-ray scattering (SAXS), inductively coupled plasma mass spectrometry (ICP-MS), nuclear magnetic resonance (NMR), and elemental analyzer (EA). Their results showed no significant difference in metal content, aromaticity and elemental composition of different cuts. Figure 2.8 shows no trend in the average alkyl chain lengths and metal content among different asphaltene cuts.

As mentioned in aforementioned part, there is still unclear issue about what chemical or physical properties of asphaltenes play an important role on aggregation

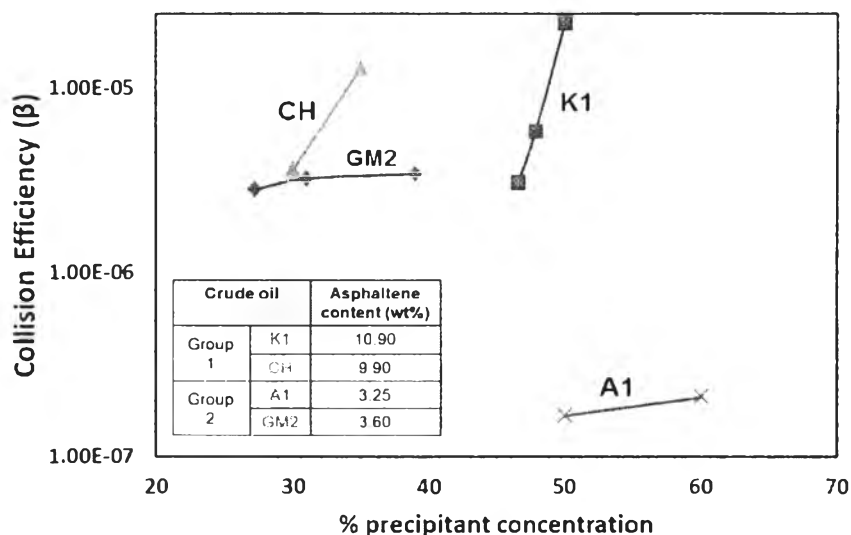


tendency of asphaltenes. Another work of Maqbool studied the evolution of aggregate asphaltenes from centrifugation experiments. They established new approach to identify the collision efficiency by using the geometric population balance and Smoluchowski kernel (Maqbool *et al.*, 2011). Extensive studies from Prof. H. Scott Fogler research group had evaluated the collision efficiency of four different crude oils, containing different asphaltene concentrations, as a function of heptane concentration. As can be seen in Figure 2.9, collision efficiencies of CH and K1, which contain high asphaltene-contents, increase significantly when the precipitant concentration increases compared to the low asphaltene-content crude oils (A1 and GM). This finding indicated that effect of asphaltene concentration might have an influence on their aggregation behavior.



**Figure 2.8** (a) average alkyl chain lengths and (b) metal contents for different asphaltene cuts (Somkhan, 2013).

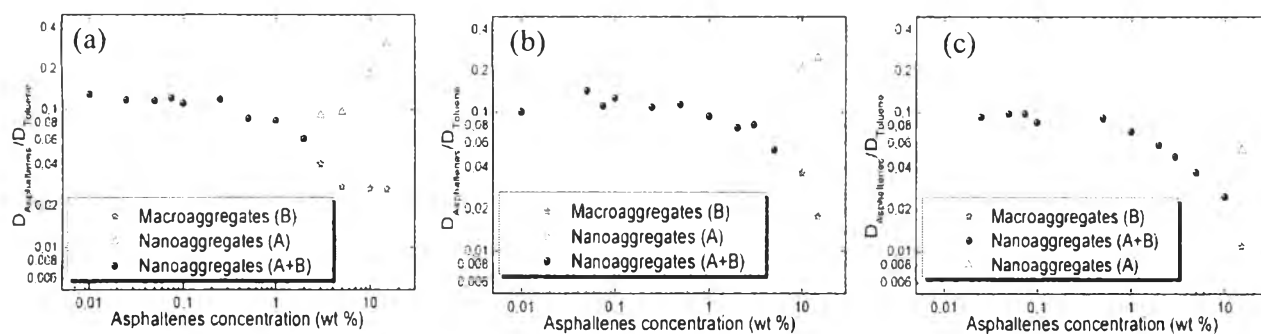
There is an interesting work performing experiments regarding the effect of chemical composition on asphaltene aggregation (Durand *et al.*, 2009). They used two-dimensional NMR spectroscopy (DOSY) to investigate the differences in macrostructure of three asphaltenes extracted from different crude oils (Athabasca, Maya and Buzurgan) by measuring their relative diffusivity in toluene.



**Figure 2.9** Collision efficiency of asphaltenes extracted from various origins vs. percentage of precipitant concentration.

The extracted asphaltenes were dissolved in toluene-d8 to generate solutions with a wide range of asphaltene concentrations. Their results, as shown in Figure 2.10, demonstrated that there was separation two classes of asphaltene aggregates: one diffusing quickly and other diffusing more slowly. In dilute regime, Maya and Buzurgan asphaltenes have similar self-diffusion while Athabasca asphaltenes have smallest diffusivity. At high concentrations (beyond 0.5 wt% for Maya and Athabasca asphaltenes and beyond 0.25 wt% for Buzurgan asphaltnes), a decrease in diffusion coefficient of those asphaltenes was observed. Moreover, the favored intermolecular interactions generate the phenomena which some asphaltenes molecules have a tendency to aggregate while some small aggregates remain in the solution. Their findings showed that aggregation behavior of those three types of asphaltenes might be dependent upon their chemical structure and the concentration of asphaltenes.

Additionally, extensive study of Haji Akbari *et al.* (2014) investigated the effect of asphaltene concentration by performing onset experiments of model mixtures containing different concentration of asphaltenes. Two types of asphaltenes, K1 and B1, were used in their study. Their microscopy results for both types of asphaltenes indicated that aggregation rates decrease with increasing asphaltene concentration. They believe that observed trend causes by an increase of viscosity



**Figure 2.10** Relative diffusivities of (a) Buzurgan, (b) Maya and (c) Athabasca asphaltenes, as a function of asphaltene concentration in toluene-d8 (Durand *et al.*, 2009).

and solvency power of a mixture. This emphasizes that asphaltene concentration play an important role in controlling aggregation kinetics of asphaltenes.

Therefore, in this work, the time-based fractionation of asphaltenes at different asphaltene concentrations is used to investigate the properties of asphaltenes that could influence their aggregation behavior. The fractionated asphaltenes were characterized using SAXS and microscopy experiments.