

[Research Note]

Mechanisms of Asphaltene Aggregation in Toluene and Heptane Mixtures

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The nature of aggregation kinetics of colloidal asphaltene particles in mixture of toluene and heptane was investigated by utilizing a polarizing microscope with appropriate magnification. The concentration of asphaltene in toluene–heptane mixture varied from 1 g/l to 8 g/l. There are two main mechanisms associated with the aggregation process. These mechanisms are diffusion limited aggregation (DLA) and reaction limited aggregation (RLA). Each mechanism has its own characteristics and acts on limited values of asphaltene concentration. At the asphaltene concentrations below the critical micelle concentration (CMC), the DLA mechanism is dominant, while at concentrations above the CMC, at the initial stage of aggregation process, the RLA mechanism is observed and then the mechanism tends toward DLA (crossover behavior). It should be noted that the CMC for asphaltene in the solution is around 3 g/l.

Keywords

Asphaltene, Aggregation mechanism, Diffusion limited aggregation, Reaction limited aggregation, Critical micelle concentration, Fractal dimension

1. Introduction

Crude petroleum can be represented by three major fractions: oils, asphaltenes and resins. Oils are mixtures of saturated hydrocarbons and aromatics of moderate molecular weight. Asphaltenes are operationally defined as the non-volatile and polar fraction of petroleum that is soluble in benzene and toluene but insoluble in alkanes (*i.e.* pentane and heptane) at room temperature. This property is used for extraction of asphaltenes. The chemical structure and physicochemical properties of asphaltenes are not well understood. Several theories, models and studies have been reported for this problem but because of the fuzzy nature of asphaltene and the large number of parameters affecting asphaltene precipitation, none of them can express the properties of asphaltene and/or mechanisms of its precipitation adequately^{1,2)}.

There are two different models to describe the nature of asphaltene in the solution. The first approach is the solubility model which considers the asphaltene to be dissolved in a true liquid state. In the second approach, the colloidal model, asphaltenes are considered to be solid particles which are suspended colloiddally in the crude oil and are stabilized by large resin molecules.

According to the solubility model, asphaltene precipitation is a thermodynamically reversible process, while in the colloidal model, precipitation of asphaltene is considered to be irreversible. The kinetics of aggregation of colloidal particles has been the subject of extensive experimental and theoretical studies for many years and numerous models have been investigated for describing the cluster aggregation.

In the literature, two models for irreversible aggregation processes are described^{4)–6)}. These are the diffusion limited aggregation (DLA) and the reaction limited aggregation (RLA). According to DLVO theory⁴⁾, the fundamental property which determines the nature of cluster-cluster aggregation is the form of the interaction potential between two colloidal particles as they approach one another. Colloidal particles which are stable against aggregation have some form of repulsive interaction which prevents two approaching particles from touching and sticking together. This repulsion is often due to charged groups adsorbed on the surface of the colloidal particles, but it can also arise from other sources, such as a thin coating of polymer on the particle surface. The height of the resultant repulsive barrier (E_b) must be much greater than attractive barrier ($k_B T$) for the colloid to be stable against aggregation. If E_b is reduced, colliding particles can surmount the barrier and stick together, thus the aggregation process initiates. The rate of aggregation will be determined by

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the probability, P , in which two particles will stick upon colliding; this is determined by the height of the remaining barrier, and is given by:

$$P = \exp\left(-\frac{E_b}{k_B T}\right) \quad (1)$$

The exponential dependence of the sticking probability on E_b makes the aggregation rate very sensitive to the value of the repulsive energy barrier and a very wide range of aggregation rates can be obtained with any colloidal suspension. However, there are two characteristics limiting regimes of aggregation. Firstly, the repulsive barrier is removed completely, so that $E_b \ll k_B T$ and $P = 1$. In this case, every collision results in sticking of particles or clusters to one another, and the aggregation rate is limited solely by the time between diffusion-induced collisions. This class of aggregation is called diffusion limited aggregation (DLA). In the second regime, the repulsive barrier is reduced to only a small amount, so that $E_b > k_B T$, and P is very small. In this case, a large number of collisions are required before two particles or clusters stick to one another, which limits the aggregation rate. This regime is called reaction limited aggregation (RLA). These two regimes lead to both extremely rapid and very slow aggregation, respectively and have been recognized as such in the traditional colloid literature. It should be noted that because of the nature of the DLA and RLA, particles density in the aggregate in the case of RLA is much more than DLA process. Furthermore, the strength of the resultant bonds is much more than ($k_B T$), so the aggregation is irreversible and the clusters formed are rigid.

Aggregation process involves two characteristic times which are not dependent on cluster size⁵. These are the diffusion time (τ_D) and the reaction time (τ_R). If $\tau_D \gg \tau_R$, the aggregation kinetics is controlled by diffusion and referred to as diffusion limit aggregation. When $\tau_R \gg \tau_D$, the aggregation kinetics is determined by the rate of the reaction and referred to as reaction limited aggregation. In the case of DLA, each particle collision results in coagulation, therefore the average size of particles is proportional to the time and the aggregation rate, dN/dt , is constant. Where N is the average number of particles in an aggregate. For RLA the probability of particles sticking and hence, the aggregation rate is a function of N .

$$\frac{dN}{dt} = \left(\frac{1}{\tau_{\text{char}}}\right) N^\alpha \quad (2)$$

$$\text{In the case of DLA: } \alpha = 0 \quad N = 1 + \frac{t}{\tau_D} \quad (3)$$

$$\text{And for RLA: } \alpha = 1 \quad N = \exp\left(\frac{t}{\tau_R}\right) \quad (4)$$

By definition:

$$N = \left(\frac{R}{R_0}\right)^{d_f} \quad (5)$$

Where R_0 is an initial particle size and d_f is the fractal dimension. It is to be noted that d_f is different for each mechanism. By substituting Eq. (5) in Eqs. (3) and (4), one can obtain the following:

$$\text{DLA: } R = R_0 \left(1 + \frac{t}{\tau_D}\right)^{\frac{1}{d_f}} \quad (6)$$

$$\text{RLA: } R = R_0 \exp\left(\frac{t}{\tau_R \cdot d_f}\right) \quad (7)$$

According to Eq. (5), d_f is a parameter which makes a relationship between mean radius of the aggregate and average number of particles in an aggregate⁵. By increasing d_f , the density of the aggregate increases. Because the mechanism of the aggregation and aggregates structure is different in the DLA and RLA mechanisms, in general, d_f is different for DLA and RLA. Even in two DLA or RLA processes, because of their different aggregation rates, d_f is not the same. The average value of d_f for DLA is $d_f \approx 1.7 \pm 0.2$, and for RLA is $d_f \approx 2 \pm 0.05$ ^{5,6}.

2. Experimental Work

An asphaltenic crude oil with a specific gravity of 0.934 ($\rho_o = 0.934 \text{ g/cm}^3$) was selected from an oil reservoir in southwest Iran. The heptane asphaltene content of the crude oil is 8.3 mass%. For the experiment, five initial solutions of asphaltene in toluene (1 g/l, 2 g/l, 5 g/l, 6 g/l and 8 g/l) were prepared, and then heptane content of 55 vol% was added to the solutions as a precipitant. The threshold volume of heptane for aggregation process is 52 vol% with uncertainty of 1 vol%⁵. The mean radius of the aggregates was measured by using an "OLYMPUS BX60" polarizing microscope with the overall magnification of 1000-fold. **Figure 1** shows a photo of this microscope. It has an upper lens with 10-fold magnification, a lower lens with 100-fold magnification and an overall 1000-fold magnification. By using the camera which is connected on top of this microscope, it is possible to monitor the aggregated asphaltene particles.

3. Experimental Results and Discussion

Figure 2 shows the mean radius of particles as a function of time for 1 g/l and 2 g/l of asphaltene in solution which are below the critical micelle concentration (CMC). The CMC for asphaltene in solution is around 3 g/l⁷. The solid curves have a power trend line Eq. (6), which represents DLA mechanism. The characteristic time (τ_D) and the fractal dimension (d_f) for each concentration are shown in **Table 1**. The val-

ues of d_f are acceptable and agree with the known result in the literature ($d_f \approx 1.7 \pm 0.2$). It is clear that, the value of d_f increases, as the concentration of asphaltene increases in solution.

Figure 3 shows the mean radius of particles as a function of time for 5 g/l, 6 g/l and 8 g/l of asphaltene in the solution, which are above CMC. In this case the mean radius of the asphaltene aggregations increases exponentially with time which can be fitted to Eq. (7). These solid lines that have completely different trend show that the dominant mechanism of aggregation is RLA for asphaltene concentration above CMC, but as

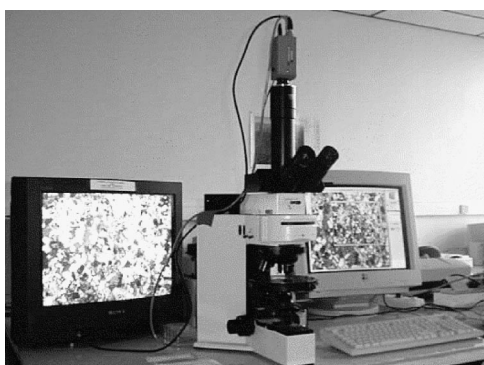
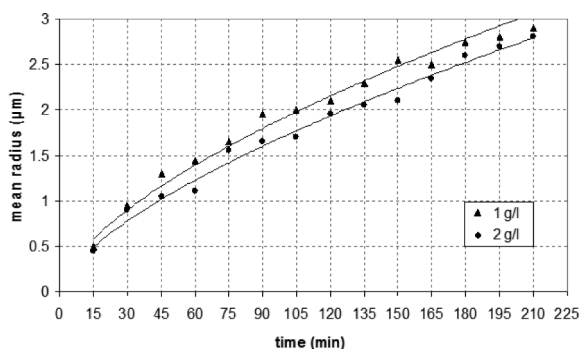


Fig. 1 The "OLYMPUS BX60" Polarizing Microscope



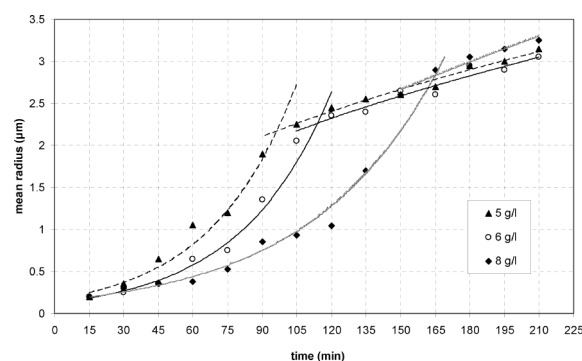
The solid curves represent the power law (representing DLA).

Fig. 2 Mean Radius of Aggregates as a Function of Time for 1 g/l and 2 g/l of Asphaltene in Toluene upon Adding 55% of Heptane

time elapses, the mechanism of aggregation changes and tends to DLA. This change is known as crossover behavior. It is concluded that the RLA mechanism controls the aggregation process for longer period of time by increasing the asphaltene concentration. Conversely, as **Fig. 3** shows the length of time for acting of DLA mechanism decreases as the asphaltene concentration increases. The characteristic time (τ_R) and initial radius of aggregates (R_0) are shown in **Table 1**.

The RLA rate slows down by increasing asphaltene concentration, because at a concentration of asphaltenes in toluene lower than the CMC, the aggregates are formed from elementary asphaltene particles and the character of the aggregation is determined by the diffusion of aggregates. Above the CMC, the aggregates are formed from micelles. As the asphaltene concentration increases, the micelles become larger and the potential barrier (E_b) becomes higher. This is the reason for the decrease in RLA rate by increasing the asphaltene concentration in solution.

Both diffusion and reaction characteristic times (τ_D and τ_R) are a function of asphaltene concentration in the solution. **Figure 4** roughly depicts this dependency and shows that, in DLA, τ_D decreases by increasing the asphaltene concentration in solution, on the other hand,



The solid curves represent the exponential law (representing RLA) and power law (representing DLA) — crossover behavior.

Fig. 3 Mean Radius of Aggregates as a Function of Time for 5 g/l, 6 g/l and 8 g/l of Asphaltene in Toluene upon Adding 55% of Heptane

Table 1 Parameters which are Associated with Asphaltene Aggregation Mechanisms in Toluene and Heptane Mixture

| | Concentration [g/l] | Heptane [vol%] | R_0 [μm] | τ_{char} | d_f |
|-----|---------------------|----------------|-------------------------|----------------------|-----------------|
| DLA | 1 | 55 | 0.1 ^{a)} | 1.3 | 1.53 |
| | 2 | 55 | 0.1 ^{a)} | 0.93 | 1.61 |
| RLA | 5 | 55 | 0.16 | 18.6 | 2 ^{b)} |
| | 6 | 55 | 0.13 | 19.7 | 2 ^{b)} |
| | 8 | 55 | 0.15 | 28.2 | 2 ^{b)} |

a) fixed for 1 g/l and 2 g/l asphaltene concentration.

b) fixed for 5 g/l, 6 g/l and 8 g/l asphaltene concentration^{5),6)}.

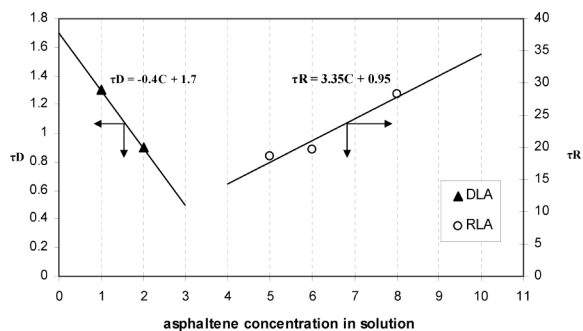


Fig. 4 Characteristic Times (τ_D) for DLA and (τ_R) for RLA as a Function of the Asphaltene Concentration in Solution for 55 vol% of Heptane

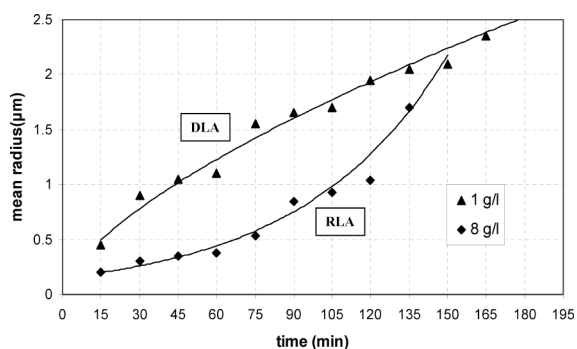


Fig. 5 Behavior of Aggregation Kinetics for Two Initial Asphaltene Concentrations

τ_R increases because of the greater effect of RLA in higher asphaltene concentration.

Figure 5 graphically indicates the behavior of aggregation kinetics for two initial asphaltene concentrations. As shown, the rate of aggregation in DLA is much higher with respect to RLA; because in DLA mechanism, every collision results in sticking of particles to one another and producing larger aggregates; but for the RLA case, a large number of collisions are required before two particles or clusters stick to one another, which limits the aggregation rate.

4. Conclusions

In kinetic aggregation point of view, there are two

main mechanisms that affect asphaltene aggregation process; these are diffusion limited aggregation (DLA) and reaction limited aggregation (RLA). Each mechanism has its own characteristics and acts on limited values of asphaltene concentration. DLA is dominant in asphaltene concentrations below the CMC, while above CMC, RLA acts on initial stage of aggregation and then the aggregation is controlled by DLA (crossover behavior).

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Nomenclatures

- d_f : fractal dimension
 dN/dt : aggregation rate
 E_b : repulsive barrier
 $k_B T$: attractive barrier
 N : average number of particles in an aggregate
 R_0 : an initial radius of particle
 R : radius of particle
 <Greeks>
 τ_D : diffusion time
 τ_R : reaction time
 ρ_o : density of oil

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要 旨

トルエン-ヘプタン混合溶媒中におけるアスファルテン凝集機構

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コロイド状アスファルテン粒子のトルエン-ヘプタン混合溶媒中での凝集速度の性質を適切な倍率の偏光顕微鏡を用い調べた。トルエン-ヘプタン混合溶媒中のアスファルテン濃度は1 g/l ~ 8 g/lとした。アスファルテンの凝集過程には二つの機構、拡散律速 (DLA) と反応律速 (RLA) が関与していた。これらの過程はアスファルテンの一定の濃度範囲で固有の特性と挙

動を示した。アスファルテン濃度が限界ミセル濃度 (CMC) より低い場合は DLA 機構が優勢であったが, CMC より高い場合は初期の凝集段階では RLA 機構が観測され, その後, 遷移状態を経て DLA 機構に移った。アスファルテンの CMC は約 3 g/l であった。

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