

Asphaltene Aggregation in Hydrocarbon Solutions Studied by Photon Correlation Spectroscopy

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Photon correlation spectroscopy has been used for studying the processes of asphaltene aggregation and flocculation in hydrocarbon solutions. The kinetics of asphaltene flocculation and the stability of asphaltene aggregates are strongly affected by the nature of the solvent. A simple theoretical model has been developed in order to interpret the experimental results.

Introduction

Asphaltenes are broadly defined as the nonvolatile fraction of a crude oil that is insoluble in *n*-heptane.¹ This fraction contains mixed paraffin–naphthene–aromatics in polycyclic structures plus sulfur, oxygen, and nitrogen derivatives. Yen et al.^{2–4} proposed a structural model of solid asphaltene particles made of stacks of a few aromatic sheets surrounded by some aliphatic chains. In the liquid phase, there is probably a colloidal polydispersion in both size and shape. In recent years, the colloidal structure of asphaltene solutions was a subject of intensive study by X-ray and neutron scattering,^{5–7} dielectric spectroscopy,⁸ and luminescence analysis.⁹ However, the processes near the onset of incipient coagulation and the precipitation kinetics have not been studied so well.¹⁰ These processes are of great importance for many applications such as deasphaltization, catalysis, bitumen technologies, etc.

In this paper we present the results of a study by photon correlation spectroscopy of the coagulation kinetics of asphaltene aggregates in mixtures of a solvent (toluene) and a precipitant (*n*-heptane). Of course, the process of asphaltene flocculation depends on many factors (e.g., the nature of the solvent/precipitant system). It is clear that the flocculation processes in crude oils can be strongly different from those observed in our model experiment.²¹ However, to understand the basic rules of the flocculation behavior of asphaltenes, it is convenient to use the simplest model system toluene/heptane.

Experimental Section

PCS Technique. We have studied asphaltene aggregation and flocculation by photon correlation spectroscopy (PCS). Nowadays, it is the most reliable and precise method for sub-micron particle sizing in optically transparent liquids.¹¹ We have modified the optical scheme of this method in a manner which allows us to use PCS for almost nontransparent (“black”) liquids.

PCS is based on the dynamic light scattering phenomenon. A laser beam passes through a liquid dispersion. A small fraction of the light scatters on the disperse particles, which are moving in the liquid as Brownian particles. The light scattering spectrum is broadened as compared with the laser

line. The line width for the scattered light Γ is connected with the diffusion coefficient of particles D by the following equation:

$$\Gamma = Dk^2 \quad (1)$$

where $k = (4\pi n/\lambda) \sin(\Theta/2)$, n is the refractive index, λ is the laser wavelength, and Θ is the angle of scattering.

Using the Einstein–Stokes equation, which describes the diffusion of Brownian particles in viscous media, one can calculate the particle radius R ¹²

$$R = k_B T / 6\pi\eta D \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature, and η is the viscosity of the continuous medium.

These relationships are valid for the case of uniform, rigid, and spherical particles. In principle, the PCS technique allows to obtain information about the particle size distribution, particle shape, particle interactions, etc. However, in the case of scattering in nontransparent liquids, we can determine only a mean particle size, because of rather large experimental errors.

Measurements of asphaltene flocculation were carried out both in the Institut Français du Pétrole (IFP) and in the Oil and Gas Research Institute (OGRI) of the Russian Academy of Sciences. In both institutions identical photon correlation spectrometers were used, which were designed and produced by OGRI and GVIDON Ltd. (Russia).

A scheme of our experimental setup is presented in Figure 1. We used a He–Ne laser with a maximum light beam power of 25 mW. For many asphaltene samples which were characterized by a strong light absorption, it was necessary to attenuate the incident beam intensity down to an admissible level. This level was determined by the necessity to avoid the laser heating of the liquid, which induces a parasitic thermoconvective phenomenon known as “thermal lens”. Square sample cells closed by a Teflon plug were placed into the thermostat. For thermostabilization, we used a circulating water pump system. The temperature stability was better than 0.1 K. Scattered light was received by a photon counting system including the receiving optics, photomultiplier tube, and amplitude discriminator. From photon counting system single electron pulses came to a multichannel real-time correlator. For our measurements we used two different correlators. The first one was a 4-bit,

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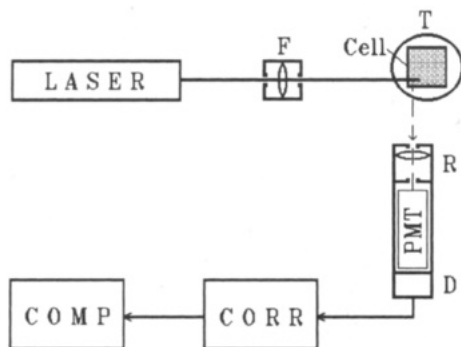


Figure 1. Scheme of the photon correlation spectrometer: F, focusing unit; T, thermostat; R, receiving optics; PMT, photomultiplier tube; D, amplitude discriminator; CORR, multichannel correlation; COMP, IBM PC.

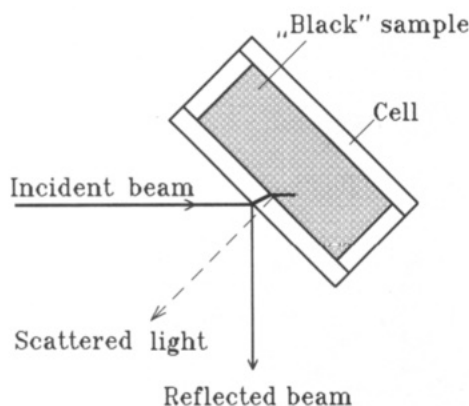


Figure 2. Modified optical scheme for particle size measurements in non transparent liquids.

64-channel correlator assembled in a separate mainframe and connected with an IBM PC 386 computer. The second one was an original single-board correlator.^{13,14} It is a 8-bit, 72-channel full hardware correlator operating in both linear and logarithm multi-tau time scale. This correlator has been made as a single PC board fitted for a standard IBM slot. Our original software provides a reliable control of the setup and an effective real-time processing of experimental data.

For size particle measurements in "nontransparent" liquids we have designed a special light scattering geometry (Figure 2). In this geometry the scattered light is collected from the input region. A rectangular sample cell is placed at an angle of 45° with respect to the incident laser beam. The optical axis of the multiplier is normal to the front plane of the sample cell.

Sample Preparation. For the study we used three different asphaltene samples extracted at IFP from Arabian and Venezuelan crude oils. Toluene was used as a solvent and *n*-heptane as a precipitant. Both toluene and *n*-heptane were of chromatographic quality.

At first we prepared a 10 g/L asphaltene solution in toluene. This was performed in a nitrogen atmosphere (without oxygen). All experimental samples at different concentrations were prepared from this primary solution. All liquids and solutions were filtered through Millipore filters of pore diameter 0.47 in order to avoid parasitic dust and insoluble impurities.

Experimental Procedure. The overall procedure for the light scattering measurements was rather conventional, but with several important exceptions. Solutions for the study (usually containing 1 g of asphaltene per liter of toluene) were prepared by diluting the primary solution directly in the sample cell. The concentrations chosen for the study were slightly below cmc in good solvents.^{8,9} After the onset of the concentration equilib-

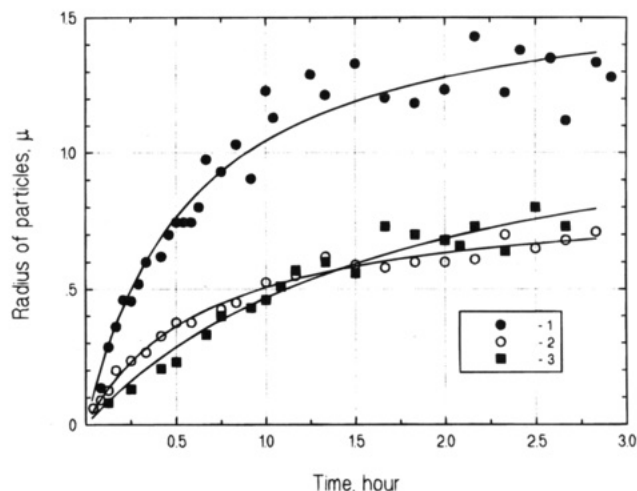


Figure 3. Initial stage of flocculation for asphaltenes of different origins in solvent/precipitant mixtures slightly above the threshold: 1, Arabian Light in 35/65 toluene/heptane mixture; 2, Boscan in 25/75 toluene/heptane mixture; 3, Arabian Heavy in 35/65 toluene/heptane mixture.

rium we added the necessary amount of heptane, shook the cell for 10–15 s, and placed it into the thermostat. From this moment we began monitoring the size of asphaltene aggregates during their growth.

Results and Discussion

The flocculation of asphaltenes in toluene–*n*-heptane mixtures depends on the origin of asphaltenes, their concentration, and the toluene/*n*-heptane ratio. At low concentration of *n*-heptane the flocculation is not observed. When the concentration of *n*-heptane reaches some threshold value, the flocculation starts. Above this point we observed the appearance of asphaltene aggregates and their growth with time. The flocculation threshold concentration for our samples (1 g of asphaltene per liter of toluene) was 50–70 vol % *n*-heptane depending on the origin of asphaltene. Since an asphaltene is not an individual substance but a multicomponent mixture, the threshold can be hardly defined as a certain toluene/*n*-heptane ratio. The kinetics of flocculation slightly above the threshold for asphaltenes of three different origins is shown in Figure 3. The process of flocculation is reversible: excess of toluene leads to dissolution of the flocs.

We can distinguish two processes in the asphaltene flocculation which can be separated by a slight shaking. Without shaking the process of flocculation goes on continuously by forming fractal-like flocs of several microns size with a very loose structure. Above a size of 1.5–2 μm the growth of flocs is accompanied by sedimentation, which prevents the measurement of their true size in the precipitant. Nevertheless, it is interesting to note that just before the ultimate sedimentation the floc size is of the order of 4–5 μm (2 μm radius) close to that of fractal-like diffusion limited aggregates observed by atomic force microscopy on a mica surface by Prayer¹⁵ (see also ref¹⁶). Such flocs can form fragile fractal structures in the precipitate.

The fractal aggregates are very unstable: a slight shaking easily destroys them, leading to the formation of particles of a very stable size (of order of 1 μm). We will refer to these particles as *basic aggregates*. The kinetics of formation of the basic aggregates is shown in Figure 4. We underline that the basic aggregate size is very stable under shaking; however the formation of fractal flocs restores immediately after the shaking stops (Figure 5). One can define the characteristic time of formation of the basic aggregates as the time when the particle

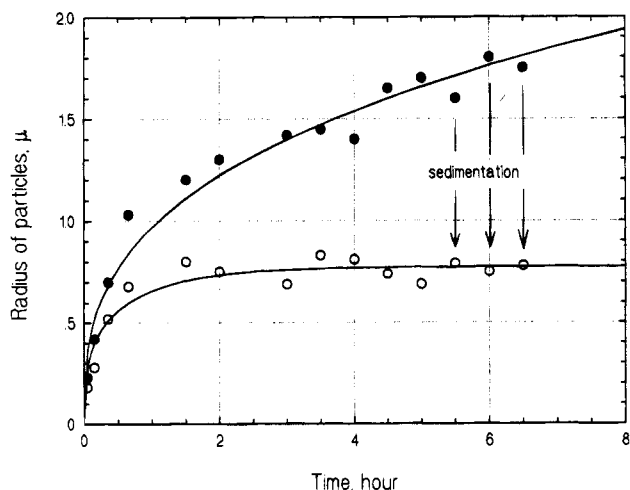


Figure 4. Two mechanisms of asphaltene flocculation in toluene/heptane solution (1 g/L Arabian Light in 35/65 mixture). Closed circles correspond to the formation of fractal aggregates and open circles to the formation of basic aggregates. Solid lines correspond to theoretical fits by eqs 7 and 10.

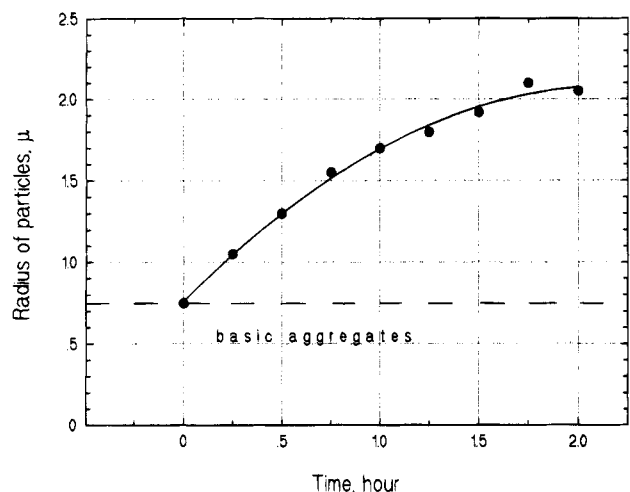


Figure 5. Fractal aggregate formation (1 g/L Arabian Light in 30/70 mixture). Zero time is the moment when shaking stops.

size is being saturated. It is about 1 h depending on the origin of asphaltenes and their concentration, and it rapidly decreases on decreasing the toluene/*n*-heptane ratio (increasing the concentration in *n*-heptane) (see Figure 6). The reverse kinetics of dissolution of the flocs is shown in Figure 7.

The analysis of experimental data shows that the kinetics of aggregation–flocculation of asphaltenes can be roughly divided into three stages. The first one is a nucleation stage corresponding to the formation of asphaltene clusters of critical size. This stage (of the order of several minutes) can be observed only in the case of small excess of heptane over the threshold. During the second stage these clusters grow into the basic aggregates mainly by absorbing the asphaltene “monomers” and small micelles from the solution. The third stage can be associated with formation and growth of ramified flocs which are made up from the basic aggregates and have apparently a fractal structure.

During the first stage, supercritical asphaltene clusters appear in the system, with a rate which is strongly dependent on the vicinity to the threshold.¹⁷

The onset of the second stage reveals itself in the appearance of aggregates with a size well measurable by PCS (approximately 0.05 μm). It means that by this time there is enough clusters of this size to be detected. From this time on we are

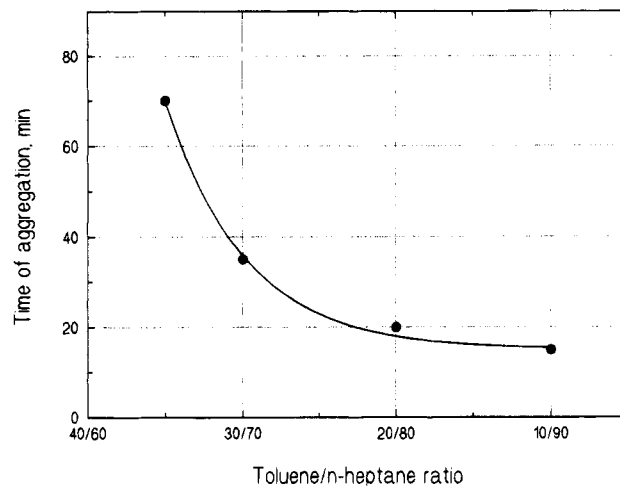


Figure 6. Characteristic time of basic aggregate formation as a function of toluene/*n*-heptane volume ratio.

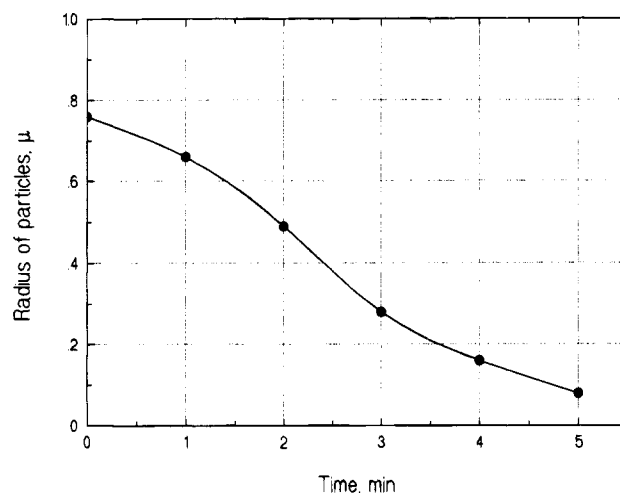


Figure 7. Kinetics of dissolution of the asphaltene flocs. An excess of 1% toluene was added into the 30/70 toluene/heptane dispersion of asphaltenes.

able to follow the slow growth of a cluster size. According to the theory of phase transitions, the relaxation of the order parameter toward the equilibrium state is determined by the equation¹²

$$\frac{d\varphi}{dt} = -\gamma \frac{d(\Delta f)}{d\varphi} \quad (3)$$

where Δf is the excess of free energy per unit volume for the nonequilibrium state, and γ is the kinetic coefficient. In our particular case the order parameter φ can be associated with the volume fraction of asphaltene clusters forming the new stable phase. In this case $d(\Delta f)/d\varphi$ is equal to $(-\Delta\mu)$, where $\Delta\mu$ is the excess chemical potential of asphaltenes in the unstable state. If the new phase is formed as a conglomerate of spherical droplets of radius R , then $\varphi = (4/3)R^3n$, where n is the number of clusters per unit volume. Equation 3 assumes the form

$$\frac{4\pi}{3} \frac{d(nR^3)}{dt} = \gamma \Delta\mu \quad (4)$$

In the assumption of exponential approach to equilibrium ($\Delta\mu = \Delta\mu_0 e^{-t/\tau}$) one obtains

$$nR^3 = n_\infty R_\infty^3 (1 - e^{-t/\tau}) \quad (5)$$

where the asymptotic radius R_∞ is the mean radius of the basic aggregates and n_∞ is their final concentration. From (4) we get

$$(4/3)n_\infty R_\infty^3 = \gamma \Delta\mu_0 \tau \quad (6)$$

The left-hand-side expression is equal (by an order of magnitude) to the molecular fraction Δc_0 of initial excess of asphaltene molecules. Thus, we obtain the simple estimate for the basic aggregates concentration: $n_\infty \sim \Delta c_0 / R_\infty^3$, which, after substituting the experimental values $R_\infty^3 \sim 10^{-12} \text{ cm}^3$ and $\Delta c_0 \sim 10^{-4}$ yields $n_\infty \sim 10^8 \text{ cm}^{-3}$.

From (6) follows the natural fact that the characteristic time τ for the formation of basic aggregates has an inverse dependence on the initial excess of chemical potential of the asphaltenes. This dependence of τ on the degree of supersaturation is illustrated by Figure 6, which shows τ plotted versus the toluene/*n*-heptane ratio (above the flocculation threshold for this system).

The explicit time dependence of the aggregate mean radius R depends on the nucleation mechanism. Suppose that the number of nucleation clusters is constant. It means that the growth of the cluster size at this stage is associated only with the adhesion of asphaltene "monomers" to the cluster surface. In this case eq 5 assumes the form

$$R = R_\infty(1 - e^{-t/\tau})^{1/3} \quad (7)$$

This equation was used for fitting the experimental data in Figure 4. The characteristic time τ obtained by this fit is equal to 0.97 h.

During the next stage, as the growth of basic aggregates is practically stopped (the supersaturation of the asphaltene solution is already very small), the main reason of cluster size growth would be the coalescence of basic aggregates due to their diffusion. Clusters formed in the process of diffusion limited aggregation (DLA) have usually a ramified fractal structure.¹⁸ In our case they should be composed, like from primary building blocks, from the basic aggregates of micron size. This explanation is supported by scanning electron microscopy⁶ and AFM.¹⁶ Moreover, some elementary estimates based on this flocculation mechanism make it even more plausible. Let us calculate the characteristic experimental time (defined as the inverse of reaction rate) in the framework of the Smoluchowski aggregation model.¹⁹ In this model, the time dependence of the reagent concentration follows the equation

$$dn/dt = -Kn^2 \quad (8)$$

where n is the concentration of asphaltene flocs and the coefficient $K = 4RD$ is the effective aggregation constant (R and D are their mean radius and diffusion coefficient, respectively). The simplified eq 8 is valid after the initial stage of the coagulation process. The characteristic time of the coagulation process is connected with the aggregation constant according to

$$\tau = 1/(Kn) \approx (4RDn)^{-1} \quad (9)$$

At the beginning of the third stage we have $R \sim 10^{-4} \text{ cm}$, and for asphaltene concentration 1 g/L we get $n \sim n_\infty \sim 10^7\text{--}10^8 \text{ cm}^{-3}$, $D \sim 10^{-8} \text{ cm}^2/\text{s}$, $K \sim 10^{-11} \text{ cm}^3/\text{s}$, and $\tau \sim 10^3\text{--}10^4 \text{ s}$, which is of the same order of magnitude as the formation time of basic aggregates and in agreement with experiment.

Using the Einstein–Stokes equation $D = k_B T / 6\pi\eta R$, one can express the coagulation constant K in terms of viscosity and

temperature: $K = (2/3)k_B T / \eta$. Taking into account a time independence of K and assuming that the coagulation to the flocs of current radius R involves all asphaltenes in a solution (i.e., $n \sim R^{-3}$), one can get from eq 8 the time dependence of the mean floc radius:

$$R = Bt^{1/3} \quad (10)$$

where the coefficient B is equal to $(Kn_0)^{1/3}R_0$ (R_0 and n_0 are floc radius and concentration at some moment of the third stage). This equation was used to fit experimental data in Figure 4; extracting B from this fit and calculating the initial concentration n_0 , we obtain the value $\sim 10^8$, the same as from the analysis of the second stage.

Let us note that the mass of fractal objects is proportional not to R^3 , but to R^{d_F} (d_F is the fractal dimension). In this case eq 10 takes the form $R \sim t^{1/d_F}$. It means that in principle the fractal dimension of asphaltene aggregates may be calculated from the experimental data. However, we have not yet accumulated enough statistics to do this.

In the case of a small mobility of aggregates, alternative mechanisms, for example that of Lifshitz–Sliozov,²⁰ should be also taken into account. The Lifshitz–Sliozov model describes the growth of the mean radius of immobile droplets of the new phase in a supersaturated solution. It corresponds to the late stage of a segregation process when the oversaturation has already become small enough due to the formation of droplets of a new phase. In this case small droplets become unstable and dissolve back to the solution, and big droplets continue to grow. It is interesting to note that the growth of the mean radius is described by the same power dependence (10) as in the DLA model; the coefficient B in the Lifshitz–Sliozov model is proportional to $(\sigma D n_0 / T)^{1/3}$, where σ is the interfacial tension. However, fitting to experimental data yields more plausible results for the DLA model. Moreover, as we have already mentioned, the scanning electron microscopy shows that the precipitate has a complex ramified fractal structure made up from the compact elementary clusters which also supports the aggregation model.

Conclusion

The different stages of the segregation of asphaltenes from a solution have been described in section 3 by simple qualitative models yielding a good agreement with experiment. What is important is that the basic parameters extracted from the different models (e.g., the aggregate concentration) are of the same order of magnitude. However, for a more detailed study of these processes one should take into account the fact that these stages should strongly interplay and different processes should take place simultaneously. On the one hand, the nucleation process should continue until there is a noticeable decrease of the oversaturation, and on the other hand, the coalescence of asphaltene clusters should be taking place in parallel with the growth of individual clusters. The relative contributions of these three mechanisms should depend strongly on their characteristic times, the mobility of clusters, and the binding energies of different aggregates and flocs.

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