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Colloidal Properties of Crude Oils Studied by Dynamic Light-Scattering[1]

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Colloidal properties and kinetics of asphaltene aggregation in three crude oils using a dynamic light-scattering method adapted to opaque fluids were investigated. The technique makes it possible to measure the size of particles suspended in nearly nontransparent liquid media. The studied native crude oils were found to have persisting colloidal particles. The observed particles are assumed to be asphaltene/resin aggregates. Using *n*-heptane as a precipitant, asphaltene aggregation kinetics in crude oils was studied. Experimental measurements of the particle size as a function of time in solutions with different oil/precipitant ratios are reported. The aggregation kinetics accelerates with increasing precipitant concentration. The oil sample with a large amount of paraffins is on the edge of instability and exhibits a slow asphaltene aggregation process without precipitant. Aggregation in the two other oils starts only at some threshold concentration of the precipitant, lasts a short time, and results in the formation of stable-in-size particles. The results obtained prove that dynamic light scattering is an effective method to test petroleum colloid stability.

KEY WORDS: aggregation kinetics; crude oil; light-scattering; petroleum asphaltenes; photon-correlation spectroscopy.

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1. INTRODUCTION

General characterization of crude oils and asphaltenes (a heavy petroleum fraction) is an important task for the petroleum industry [1]. Different crude oils exhibit an enormous range of properties impacting all phases of oil exploitation. Arterial blockage in the petroleum industry is due mostly to the deposition of heavy fractions from crude oil. Field experience [2, 3] and experimental observations [4, 5] indicate that asphaltene stability is dependent on various factors including composition, pressure, and temperature of the oil. Our research is targeted at investigation of the influence of the composition on asphaltene aggregation stability.

Crude oil is a complex mixture of hydrocarbons and heteroatomic organic compounds of varying molecular weight and polarity. A common practice in the petroleum industry is to separate the crude oil into four chemically distinct fractions: saturates, aromatics, resins, and asphaltene (SARA). Two key parameters that control the stability of asphaltene particles in a crude oil are the ratios of aromatics to saturates and resins to asphaltenes. When this ratio decreases, asphaltene particles may coalesce and form larger aggregates [6].

Analysis of experimental data indicates that formation of associates in crude oil and petroleum liquid fractions is more complicated then described by existing simple models. Non-Newtonian rheological behavior of petroleum systems (especially those with high-content asphaltenes and paraffins) suggests the presence of supramolecular mesoscopic structures. However, the physical nature of these structures is not well understood. It is commonly accepted that the mesoscopic structure formation is somehow associated with asphaltenes. In accordance with extraction procedure, asphaltenes are defined as a heavy fraction of crude oil that is completely miscible in aromatic hydrocarbons such as toluene and benzene but is insoluble in *n*-alkanes [7]. This definition is in some sense arbitrary, as the molecular structure of asphaltenes varies significantly depending on their origin, method of oil recovery, and history of extraction [8]. Attempts to find a reliable correlation between extensive data on asphaltene structures and their colloidal properties have not been successful.

We have used a dynamic light-scattering technique to investigate colloidal properties and asphaltene aggregation phenomena in crude oils.

2. METHOD AND TECHNIQUE

A compact photon-correlation spectrometer with an original optical scheme and with an original single-board correlator to perform dynamic light-scattering measurements was used in our experiments [9]. Photon-correlation spectroscopy (PCS) is commonly used to determine the size of nanoparticles in a suspension by measuring the dynamics of the light-scattering intensity fluctuations. The diffusion coefficient D of the particles is directly related to the decay rate t_c of the time-dependent correlation function. For the homodyne regime of PCS the relation between D and t_c is [10]:

$$D = 1/(2t_c k^2) \tag{1}$$

where k is the wave number of the scattered light, $k = (4\pi n/\lambda)\sin(\Theta/2)$, n is the refractive index of the solvent, λ is the wavelength of the incident light in vacuum, and Θ is the scattering angle.

The mean hydrodynamic radius of the particles R can be calculated using the Stokes–Einstein equation:

$$D = k_B T/(6\pi\eta R) \tag{2}$$

where k_B is Boltzmann's constant, T is the temperature, and η is the shear viscosity of the solvent.

Equation (2) is valid for noninteracting particles. If the particles are involved in an aggregation process, they certainly interact. However, Eq. (2) is still applicable to monitor the change of the apparent particle size if the characteristic time of aggregation is much larger than the time of measurements.

We used an original optical scheme (Fig. 1) which enables us to perform dynamic light-scattering measurements in opaque disperse petroleum systems and, in particular, to study aggregation phenomena of petroleum asphaltenes [9]. A rectangular sample cell is placed at an angle of 45° with respect to the incident laser beam emanating from a low-intensity He–Ne laser (2 mW, 632.8 nm). Strong light absorption in opaque petroleum samples may cause a thermal-lens effect, which can be easily detected by specifically looking at the correlation function. To avoid this effect, the laser beam power can be attenuated by neutral glass filters. The optical axis of the photodetecting system, operating in the photon-counting mode, is normal to the front plane of the sample cell. The scattered light is collected from the region where the laser beam enters the sample. To obtain optimal conditions for collection of scattered light and for suitable alignment of the incident laser beam, an optical plate unit was used. The position of the scattering volume can be adjusted so as to study light-scattering near the wall (not less than 0.1 mm from the wall to exclude the influence of the surface and heterodyning from stray light). Fidelity of the homodyne regime was verified by performing particle size measurements at different

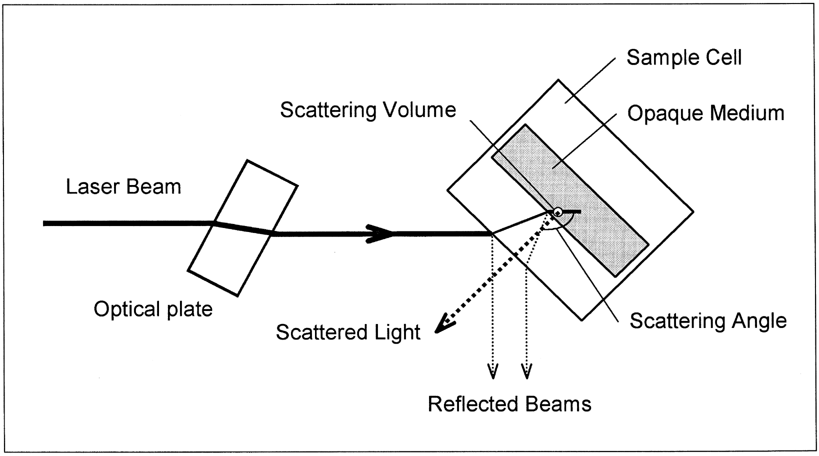

Fig. 1. Optical arrangement for dynamic light-scattering in nontransparent fluids.

distances from the wall of the sample cell. Such a scheme allows one to measure particle size in any practically nontransparent liquids. It is also important to emphasize that for opaque systems there is no problem with interpretation of dynamic light-scattering data because strong light absorption eliminates possible multiply scattered light. Standard square 4-mm-path length optical-glass cells produced by Hellma Inc. were used.

3. EXPERIMENT AND RESULTS

Three samples of crude oils (supplied by Shell) were investigated. According to information from Shell, these oils have asphaltene instability problems, and one can expect spectacular aggregation phenomena. Petroleum samples were dehydrated and filtered. No additional treatment was given to the oil samples. The SARA analysis data for the crude oils are presented in Table I. All the experiments were made under ambient conditions. *n*-Heptane, filtered through a 0.2-μm Millipore filter, was used as a precipitant. A fresh sample was prepared for each experiment. Hamilton syringes were used for sample preparation (0.2 cm^3 of crude oil for each experiment). After transferring the oil sample and the required amount of precipitant into an optical cell, the cell was shaken for several seconds and placed into the thermostat, and the measurements were then started. To obtain a correlation function of reasonably good quality, the accumulation time for each measurement lasted from 1 to 15 min, depending on the rate of the process. The total duration of each experimental run varied from 40 min to several days.

Table I. Representative SARA Values for the Crude Oil Samples

Specimen No.	Crude oil	Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	Gravity (°API)
1	Europe SkyBlue	27.13	56.72	9.4	6.75	25.3
3	Mars A-12	24.3	55.6	14.9	5.15	23.5
2	Swanson River	53.1	35.2	7.2	4.53	32.7

The experimental procedure included integral light-scattering intensity and autocorrelation function measurements. The integral light-scattering intensity is proportional to the number of particles in a scattering volume. It can be used for estimation of the concentration of particles. Two examples of measured correlation functions are presented in Fig. 2. The solid curves are fits to an exponential model. For oil samples with small particles (Fig. 3a) the quality of the correlation function is not very good, nevertheless, it is enough for reliable determination of the mean radius of particles. For large particles (Fig. 3b), the accuracy of the correlation function is essentially better but other parameters of the particle size distribution still cannot be obtained.

The viscosity of the oils and oil/precipitant mixtures was measured with a high-resolution rotational viscometer (Rheometrics Fluids Spectrometer II) at various shear rates and at the same temperatures at which the light-scattering experiments were performed. To avoid evaporation of light petroleum components during measurements, all necessary precautions were taken. In the process of measurements, *n*-heptane was gradually

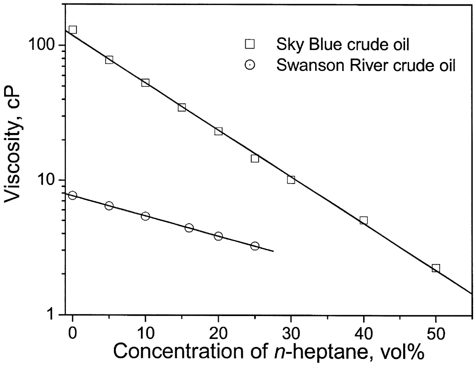

Fig. 2. Shear viscosity of oil mixtures as a function of precipitant volume concentration.

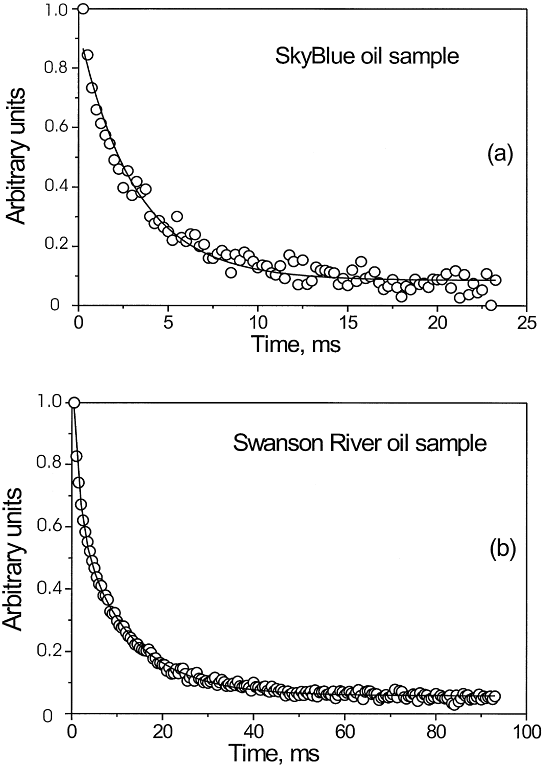

Fig. 3. An example of measured correlation functions: (a) small particles in SkyBlue oil without precipitant; (b) large particles in Unocal Swanson River oil without precipitant. Solid curves represent the fit to an exponential model.

added to oil sample and the viscosity of mixtures at different oil/precipitant ratios was obtained. Results of viscosity measurements are presented in Fig. 3. According to the classical Einstein equation for the viscosity of suspensions, the change in oil viscosity during asphaltene aggregation process is estimated to be insignificant. Even the aggregation of all asphaltenes present in a crude oil, which in fact does not occur in our experiments, would lead to viscosity changes of about 10 to 15%. The change is comparable with the accuracy of our particle size measurements and can be neglected when the size of aggregates grows by orders of magnitude. The refractive index required for calculation of the wave number was taken from the data reported in Ref. 11. The effect of the oil refractive index change resulting from asphaltene aggregation is completely negligible.

The results and discussion of the experimental investigation of colloidal properties and aggregation phenomena for three live oil samples specified by Shell as Europe SkyBlue, Mars A12, and Unocal Swanson River are presented below.

3.1. Europe SkyBlue Oil Sample

Particles with a mean radius of about 10 nm were detected in the crude oil and in a mixture of the oil with 20% of precipitant added. We observed these systems for 24 h. There was no significant change in the mean radius and the concentration of the particles. In solutions with concentrations of

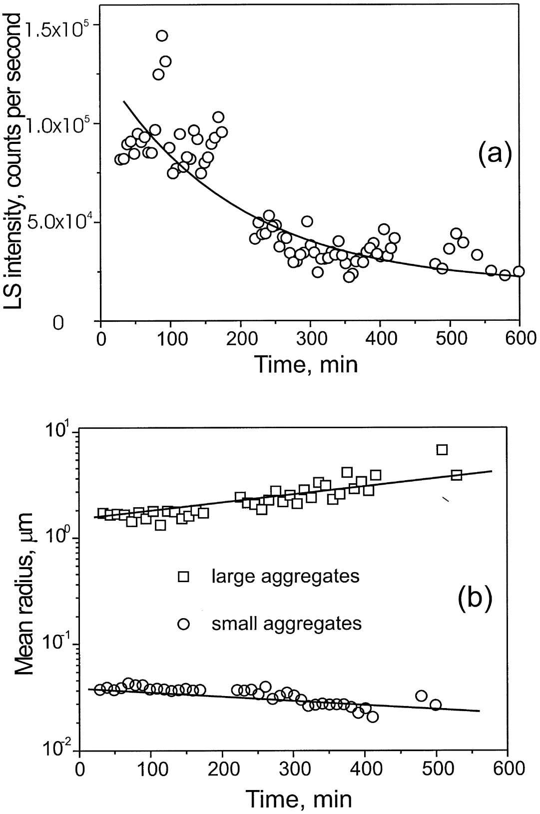

Fig. 4. Light-scattering intensity (a) and mean radius (b) for SkyBlue oil with 44% volume of precipitant as a function of monitoring time. Solid curves are fits to an exponential model.

25% volume *n*-heptane and higher, particles of two sizes were detected by measuring the correlation function on two time scales. While the small particles remained in the system, large aggregates formed. The kinetics of large aggregate formation was not observed. For a mixture of the oil with 44% volume *n*-heptane, both sizes of the particles did not change by more than a factor of two during 10 h (Fig. 4b). However, the intensity of the scattered light decreased considerably with monitoring time, which indicates a decrease in the concentration of the particles (Fig. 4a). The size of large aggregates increased with a greater amount of precipitant added (Fig. 5). Depending on the concentration of the precipitant, we were able to measure the particle size over a time period of more than 20 h for a solution with 30% volume *n*-heptane, over less then 10 h for a solution with 44% volume *n*-heptane, over less then 6 h for a solution with 49% volume *n*-heptane, and over 2 h for a solution with 53% volume *n*-heptane. After the aforementioned periods, the scattered intensity, i.e., particle concentration, became so low that we could not perform particle sizing any longer. The particles could be observed again after shaking the sample. After that, they sedimented within 1.5 h.

From the results above we may conclude that Europe SkyBlue oil has an intrinsic supramolecular structure, i.e., colloidal particles 10 nm in size. This size remains stable in both the original oil and a solution with up to 20% volume of the precipitant. Addition of the precipitant at concentrations higher than some threshold concentration of 25% volume initiates fast aggregation and formation of stable large aggregates. Eventual sedimentation follows the aggregation process, decreasing the particle concentration in the sample. The sedimentation rate observed is proportional to the aggregate size.

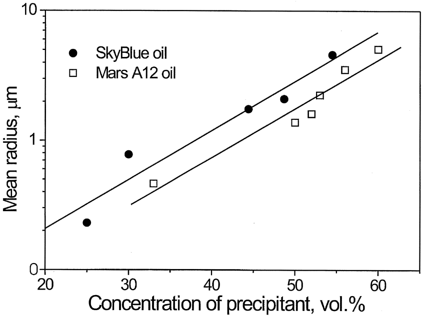

Fig. 5. Average size of asphaltene aggregates for various concentrations of precipitant for SkyBlue and Mars A12 oil samples.

3.2. Mars A-12 Oil Sample

Unlike Europe SkyBlue oil, no small colloidal particles are detectable both in the pure oil sample and in a mixture of the crude oil with small amounts of *n*-heptane, up to 20% volume. The addition of a greater amount of precipitant causes the formation of large aggregates with sizes of 0.4 μm (33% volume *n*-heptane) to 5 μm (60% volume *n*-heptane) (Fig. 5). In Fig. 6 experimental results for mixture of the oil with a 50% volume of the precipitant are presented. The concentration of aggregates remained constant with monitoring time during 25 h (Fig. 6a). The particle size did not change significantly either (Fig. 6b).

We have concluded that the aggregation phenomena in Mars A-12 oil are quite similar to those in Europe SkyBlue oil, except for the fact that an intrinsic colloidal structure in this sample is not observed.

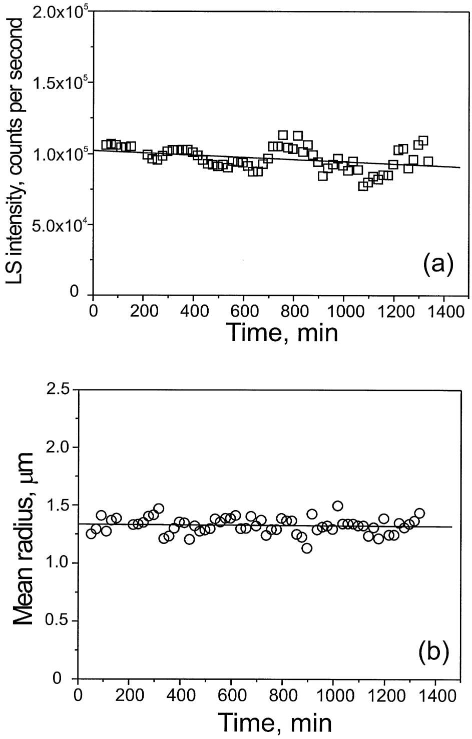

Fig. 6. Light-scattering intensity (a) and mean radius (b) for a solution of Mars A-12 oil with 50% volume of precipitant as a function of monitoring time.

3.3. Unocal Swanson River Oil Sample

Behavior of this sample differs from that described above. Extremely slow aggregation kinetics has been observed in the pure oil. During 5.5 days the effective size of the particles grew from about 0.7 to 1.6 μm. Results of two runs presented in Fig. 7 demonstrate reasonable reproducibility. We could explain this puzzling aggregation as being induced by laser radiation. However, we do not believe that such a low laser power (less than 0.1 mW) can cause such an effect. We may also speculate that the kinetics observed is related to slow restoration of some soft gel-like structure after the sample preparation procedure. Anyway, this effect is challenging and should be specially investigated.

A strong effect of aggregation in this oil was observed for any amount of precipitant added. Curves representing exponential particle growth for various *n*-heptane concentrations are shown in Fig. 8. The characteristic time of aggregation was found from the exponential fitting of the experimental curves. The characteristic time of aggregation decreases exponentially from 2300 min for an *n*-heptane concentration of 5% volume to 20 min for an *n*-heptane concentration of 25% volume (Fig. 9).

Particle size growth in mixtures with 5, 9, and 18% volume *n*-heptane involves two phases. The initial phase of the experimental data obeys a power law with an exponent close to $\frac{1}{3}$. This extremely slow process is similar to the process observed in the pure oil. The second phase of the experimental data represents exponential growth, with a characteristic time of 2300 min in the 5% mixture (Fig. 10), which can be interpreted as the reaction-limited aggregation observed earlier in toluene/heptane solutions of asphaltenes [12]. However, the initial stage of this exponential growth is

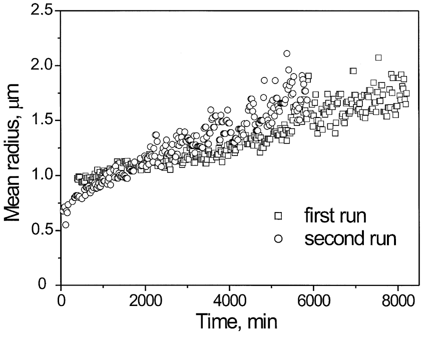

Fig. 7. Mean radius of aggregates in Unocal Swanson River crude oil without precipitant as a function of monitoring time.

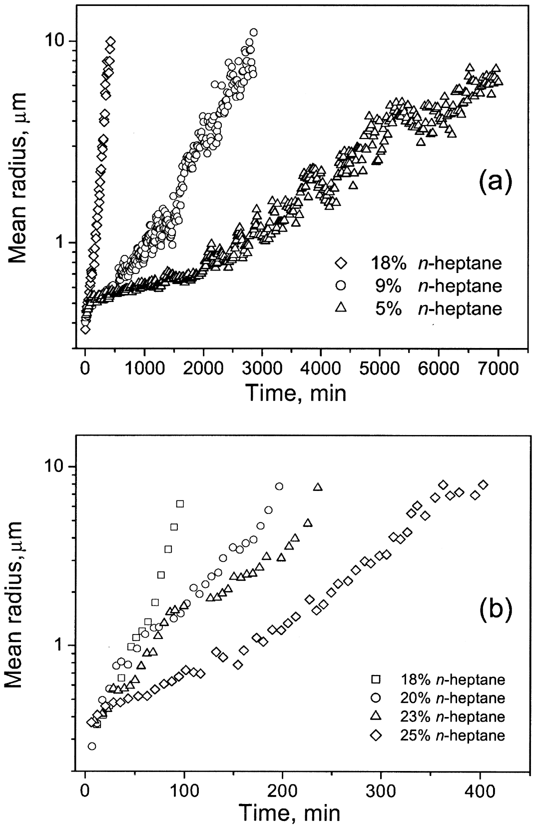

Fig. 8. Exponential growth of aggregates in solutions of Unocal Swanson River oil with lower (a) and higher (b) concentrations of precipitant as a function of monitoring time.

concealed by the power-law process, as the larger particles dominate. This overlapping area prevents us from distinguishing between these two processes with dynamic light-scattering. The intercept of these two processes is shifted to lower times with an increase in the precipitant concentration.

For this crude oil sample we could not find the threshold concentration of the precipitant. Particle size growth was observed in a solution with concentrations of *n*-heptane as low as 3%.

Unocal Swanson River oil clearly exhibits an intrinsic colloidal structure that is on the edge of instability. Mixtures of the oil and *n*-heptane show spectacular aggregation phenomena, with the rate depending on the oil/precipitant ratio. According to the SARA analysis, the content of this

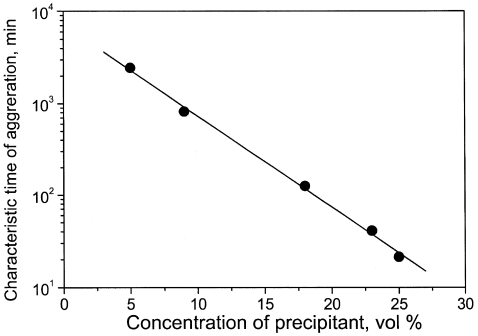

Fig. 9. Characteristic time of aggregation in Unocal Swanson River oil as a function of precipitant volume concentration.

oil is quite different from that of the other oils (large fraction of saturated hydrocarbons and paraffins; Table I). This could be a reason why the aggregation is so slow and can be easily observed.

4. CONCLUSION

Colloidal properties and kinetics of asphaltene aggregation in three crude oil samples with a dynamic light-scattering method adapted to opaque fluids have been investigated. For the first time colloidal particles

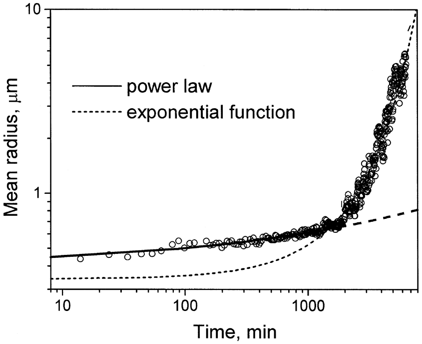

Fig. 10. Mean radius of aggregates versus monitoring time for Unocal Swanson River oil with 5% volume of precipitant. Two dynamic processes, power-law growth (solid line) and exponential growth (dashed line), are clearly seen on the double-logarithmic scale.

with sizes ranging from 10 to 700 nm in original oils were detected by the absolute method. We assume that the particles observed are asphaltene/resin colloidal aggregates. Typical aggregation kinetics, as in the model asphaltene solutions [12], was found for mixtures of Unocal Swanson River oil and *n*-heptane. Unusual behavior of aggregation was observed in the other two oils. The addition of *n*-heptane to these oils causes fast formation of large stable-in-size aggregates that sediment slowly. We plan to perform further investigation of such systems.

Our results manifest colloidal properties of original crude oils. The SARA analysis data can be helpful to predict asphaltene/resin colloid stability in crude oils. The results obtained prove that dynamic light scattering is an effective technique for real-time monitoring of petroleum colloid stability. The technique can be applied to various petroleum engineering tasks, e.g., to test the effectiveness of inhibitors of asphaltene deposition.

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REFERENCES

1. E. Y. Shue and O. C. Mullins (eds.), *Asphaltenes: Fundamentals and Applications* (Plenum, New York, 1996).
2. R. B. De Boer, Klaas Leerlooyer, M. R. P. Eigner, and A. R. D. van Bergen, *SPE Production & Facilities* (Feb. 1995), p. 55.
3. G. A. Mansoori, http://www.uic.edu/mansoori/HOD_html (1995).
4. S. I. Andersen and K. S. Birdi, *J. Colloid Interface Sci.* **142**:497 (1991).
5. J. Wang, X. Wu and O. C. Mullins, *Appl. Spectrosc.* **51**:1890 (1997).
6. O. C. Mullins and E. Y. Shue (eds.), *Structure and Dynamic of Asphaltenes* (Plenum, New York, 1998).
7. R. B. Long, in *Chemistry of Asphaltenes*, Advances in Chemistry Series, Vol. 195, J W. Bunger and N. C. Li, eds. (American Chemical Society, Washington, DC, 1981), p. 17.
8. V. Calemma, P. Iwanski, M. Nali, R. Scotti, and L. Montary, *Energy Fuels* **9**:225 (1995).

9. I. K. Yudin, G. L. Nikolaenko, V. I. Kosov, V. A. Agayan, M. A. Anisimov, and J. V. Sengers, *Int. J. Thermophys.* **18**:1237 (1997).
10. H. Z. Cummins and E. R. Pike (eds.), *Photon Correlation and Light Beating Spectroscopy* (Plenum, New York, 1974).
11. J. S. Buckley, G. J. Hirasaki, Y. Liu, S. Von Drasek, J.-X. Wang, and B. S. Gill, *Petrol. Sci. Technol.* **16**:251 (1998).
12. I. K. Yudin, G. L. Nikolaenko, E. E. Gorodetskii, E. L. Markhashov, V. A. Agayan, M. A. Anisimov, and J. V. Sengers, *Physica A* **251**:235 (1998).