ASSOCIATION AND PHASE FORMATION IN SOLUTIONS OF ASPHALTENES

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Crude oils and residual stocks, from the standpoint of colloid chemistry, are disperse systems [1]. It is believed that the asphaltenes in these materials may be present in a colloidally dispersed state [1, 2], or they may form true solutions, or they may precipitate in the form of a solid phase [1, 3]. The association of asphaltenes and their segregation in an individual phase are significant factors in petroleum refining processes and in determining the quality of the products obtained. In spite of the importance of this question, practically no information is available from direct measurements of the size of asphaltene associates in hydrocarbon solutions. It is difficult to use optical methods for this purpose because of the absorption of photons in the optical frequency range.

The present work has been aimed at measuring the dimensions (radius) of the disperse-phase particles (asphaltene associates) in certain model systems. As objects of investigation we chose the primary asphaltenes recovered from a vacuum resid produced from mixed West Siberian crudes. As the solvents we used individual hydrocarbons (toluene, cyclohexane, n-heptane).

A number of methods are available for determining the dimensions of colloidal particles. The most accurate method is photon correlation spectroscopy (PCS) [4]. It consists of determining the diffusivity D of colloidal particles by measuring the spectral composition (or correlation function) of scattered light. The diffusivity is related to the correlation time τ_c by the equation

$$DK^2=1/\tau_c$$

and to the particle radius R by the Einstein-Stokes formula

$$D=k_BT/(6\pi\eta R)$$

where $K = (4\pi n/\lambda)\sin(\theta/2)$ is the wave vector of fluctuations of the number of particles; n is the refractive index; λ is the wavelength of the incident light; θ is the scattering angle; k_B is the Boltzmann constant; T is the absolute temperature; η is the shear viscosity.

The primary advantage of the PCS method is that the dimensions of the colloidal particles are determined without any precalibration of the spectrometer. The measurements are performed without contact, essentially without any perturbation of the medium being investigated. As an intense monochromatic light source we used a laser, and as the analyzing instrument a digital correlator operating in real time. This method has been improved at the I. M. Gubkin Moscow Institute of Oil and Gas. With these improvements, it became possible to measure particle dimensions in essentially opaque and strongly absorbing liquids such as solutions of asphaltenes at high concentrations. The range of measurements extends from 2 nm up to several μm; the error of measurement is less than 5%.

The dimensions of asphaltene particles in low-transparency media were measured in an experimental unit that is shown schematically in Fig. 1, the samples being contained in flat cuvettes with a thickness of approximately 1 mm. For convenience in tuning and in calculating corrections to the scattering angle, the cuvette was positioned normal to the optical axis of the photoreceiver (FÉU-79 photomultiplier in the photon count mode). Depending on the particular task being accomplished, one of three different lasers was used: LGN-50, LG-38, and LG-79-1. The laser beam power was adjusted according to the allowable warmup of the sample and was held constant during the time of measurement (deviation no greater than 0.05%). The local warmup of the sample was no greater than 0.1°K.

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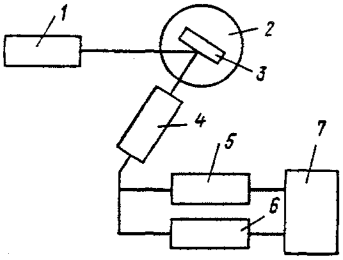

Fig. 1. Block diagram of photon correlation spectrometer: 1) He–Ne laser; 2) thermostat; 3) cuvette with sample; 4) FÉU-79 photomultiplier; 5) correlator; 6) frequency meter; 7) microcomputer.

TABLE 1

Asphaltene concentration, wt. %	Dimension (nm) of associates in indicated solvent	
	toluene	cyclohexane
2	5,0	2,0
4	5,0	2,0
6	10,0	10,0
10	13,5	13,5

The absence of any convective flows due to warmup was monitored visually on the basis of the shape of the transmitted beam. The cuvette containing the sample was placed in a thermostat in which the temperature was held within 0.02°K. The autocorrelation function of light scattering was measured by means of a digital 64-channel 3-bit correlator operating in conjunction with a DVK-1M computer. The spectrometer software made it possible to process the results from the measurements by the nonlinear least squares method. In evaluating the degree of polydispersity of the sample, the experimental data were approximated by a one- and two-exponential model or by the method of cumulants.

Studies of the behavior of asphaltenes in pure solvents differing in nature (toluene and cyclohexane) showed that the associate dimensions are practically the same in the two solvents (Table 1). The error in determining the dimensions increases with decreasing dimension, the error amounting to 30% at dimensions of 2-3 nm. We also determined the dimensions of the asphaltene associates in a mixture of a solvent and a precipitant. As the solvent we used toluene, and as the precipitant n-heptane. The samples were prepared as follows: A weighed sample of the asphaltenes was dissolved in toluene, and then n-heptane was added to the solution immediately before the measurements.

It was established that when the toluene concentration is reduced from 100% to 50% with a corresponding increase in the n-heptane concentration from 0 to 50%, the asphaltenes (at a 0.1% concentration) still form true solutions (diffusivity $D \approx 10^{-9}$ m^2/sec) and their dimension is on the order of 1 nm. When the toluene concentration is reduced from 50% to 10% with a corresponding increase in the n-heptane concentration from 50% to 90%, the asphaltenes are found to be in a colloidally disperse state or in the form of a precipitated disperse phase.

The kinetics of asphaltene coagulation in this solvent/precipitant system were studied in relation to the percentage ratio of system components. It was established that the asphaltene coagulation rate is related to the percentage content of the solvent/precipitant mixture. The lowest rate of precipitation of asphaltene associates was observed in the system consisting of 50% toluene and 50% n-heptane. The kinetics of asphaltene coagulation in the mixture consisting of 30% toluene and 70% n-heptane are shown in Fig. 2. The dimensions of the precipitated asphaltenes are shown in Fig. 3 as a function of the solvent/precipitant percentage ratio. The dimensions of the asphaltene associates remained unchanged after settling of the mixture for several days.

The following explanation can be offered for the processes of coagulation and subsequent precipitation of asphaltenes in the toluene/heptane system as the n-heptane concentration x_H is increased. In straight toluene ($x_H = 0$), the asphaltenes are well dissolved and are

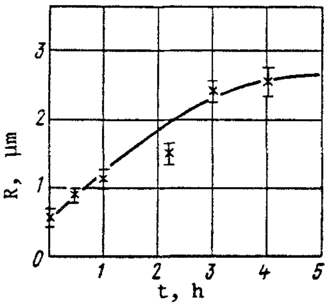

Fig. 2

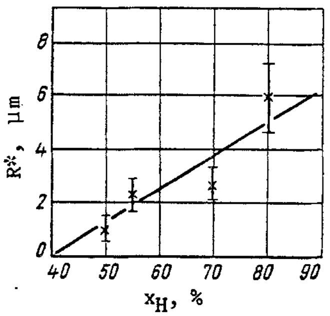

Fig. 3

Fig. 2. Timewise change in dimension R of asphaltene associates upon coagulation in mixture of 30° toluene and 70% n-heptane.

Fig. 3. Dimension R^* of particles of precipitated asphaltenes as a function of n-heptane concentration x_H in mixture with toluene solvent.

dispersed essentially to molecular dimensions ($a \leq 1$ nm). The dimensions R of the asphaltene particles are considerably greater than the dimensions a_T of the toluene molecules; therefore, in describing these processes, we can introduce the magnitude of the effective interfacial tension σ^* at the asphaltene/toluene interface. According to what has been set forth above, σ^* must satisfy the criterion of lyophilicity [4]

$$\sigma^* \leqslant \sigma_C = \gamma a^{-2} \tag{1}$$

where σ_c is the critical surface tension, above which a system of particles with dimensions of approximately a will lose stability and begin to coagulate; $\gamma \propto \ln (N_T/N_A)$; N_T, N_A are the respective numbers of particles of solvent and asphaltenes.

The asphaltene particles are lyophilic in relation to toluene molecules (and hence, in dilute solutions, the formation of asphaltene associates is highly improbable) and are lyophobic in relation to n-heptane molecules. On this basis, we can write

$$\sigma^*_{A-T} < \sigma_C, \qquad \sigma^*_{A-H} > \sigma_C$$

As n-heptane is added to the asphaltene/toluene system, the value of σ^* changes from σ^*_{A-T} at $x_H = 0$ to σ^*_{A-H} at $x_H \approx 100\%$. It can be stated that $\sigma^*(x_H)$ increases monotonically until the condition of stability (1) is violated at some value of x^*_H, i.e.,

$$\sigma^*(x^*_H) = \sigma_C$$

After this, coagulation of the asphaltenes begins. With increasing x_H, the shielding of the asphaltenes by toluene molecules is weakened; i.e., more and more of them enter into interaction with n-heptane (toluene and n-heptane have good mutual solubilities, i.e., are lyophilic in relation to each other). In this connection, the effective number of toluene molecules surrounding the asphaltene particles is reduced. When $x_H > x^*_H$, we observed coagulation with subsequent precipitation. The dimensions of the precipitated particles remained practially unchanged, depending only on the n-heptane concentration (Fig. 3).

The observed effect can probably be explained as follows. With $x_H > x^*_H$, the condition of lyophilicity (1) is violated, and the particle size begins to increase in the process of coagulation. This process is accompanied by a decrease in the total area of the asphaltene/solvent interface, since $s \propto 1/R$. When this occurs, an ever-decreasing number of toluene molecules are required for shielding of the asphaltene particles. Thus, with increasing R (under otherwise equal conditions), the surface energy decreases. The same effect is produced by the decrease in surface curvature, since the magnitude of σ^* depends on R.

We may get the overall impression that an increase in particle size will lead to restoration of the lyophilicity criterion (1) and thus will hinder coagulation. However, it follows from condition (1) that the critical interfacial tension σ_c will also decrease with increasing particle dimension: $\sigma_c(R) \propto 1/R^2$.

Therefore, a retardation and interruption of the coagulation process, depending on the difference $\Delta\sigma = \sigma^*(R) - \sigma_C(R)$, is possible in the case in which $\sigma^*(R)$ decreases more rapidly than $1/R^2$. (Obviously, such a dependence of σ^* can be expected only within a limited region of heptane concentrations $x_H^* < x_H < x_H^{**}$. With $x_H > x_H^{**}$, the dipole effect will predominate. The experimental data suggest that within the range of concentrations x_H that were investigated, a coagulation retardation effect is observed.)

On the basis of our experimental data, we can state that for the selected concentration of asphaltene (0.1%), $x_H^* \approx 50\%$. At this concentration, the coagulation proceeds very slowly. The kinetics of growth of associates in the process of asphaltene coagulation with $x_H > x_H^*$ were investigated for the concentration $x_H = 70\%$. As can be seen from Fig. 2, the comparatively rapid increase in associate dimensions, which can be approximated by a power relationship of the type $R(t) \propto t^{\alpha}$ (where t is the coagulation time; α is a certain parameter less than unity), is replaced by a slower increase in R(t) when the associate dimension reaches a value $R \approx 2.5$ μm, indicating a coagulation retardation effect. Any investigation of the subsequent growth of the associates is much more complicated, since the observation time becomes comparable to the precipitation time.

By means of measurements of the dimensions of associates that had been precipitated for several days, these measurements being made after shaking the mixture, it was shown that the value of R subsequently reaches a certain limiting value R^* that is characteristic for each concentration of precipitant x_H. The plot of $R^*(x_H)$ illustrates the monotonic increase of R^* with increasing x_H.

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MECHANISM OF ACTION OF ANTIOXIDANT ADDITIVE PAIR

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The quality of turbine oils, at the existing levels of production technology and crude oil sources, is improved by the use of various additives. In particular, so-called antioxidant pairs have been used, these pairs having a synergistic effect. The following pairs of antioxidant additives are being used in turbine oils for Soviet power plant applications: p-hydroxydiphenylamine and dithioaniline; phenyl-β-naphthylamine and anthranilic acid [1]. Experimental-commercial tests have been performed on oils containing the combination of Ionol [2,6-di-tert-butyl-4-methylphenol] and betol [β-naphthyl salicylate] [2], and also on Ionol-quinizarin and Ionol-dithioaniline combinations.

Here we are reporting on an investigation of the mechanism of action of an additive pair consisting of zinc dialkyldithiophosphate (DF-11) and a mixture of C_{17}-C_{21} aliphatic amines. These oils were tested in a pharmaceutical white oil, in a turbine oil base stock produced at the Fergana refinery, and in commercial oil from the Baku refinery. The pharmaceutical white oil was first purified by extraction, shaking the sample with a 10% aqueous sodium hydroxide solution, followed by water-washing the oil to neutral reaction of the water extract, drying by paper filtration, and then (immediately before used) treating with freshly calcined silica

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