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PHASE BEHAVIOUR OF ASPHALTENES IN PETROLEUM DISPERSE SYSTEMS

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Abstract

Experiments with crude oils, toluene solutions of oils and of vacuum residua have revealed an unexpectedly low solubility limit of asphaltenes in petroleum-based fluids. Namely, aggregation of monomers into molecular aggregates begins at asphaltene concentrations not exceeding 1-2 mg/l, while massive formation of asphaltene nanocolloids occurs at 60-100 mg/l. Moreover, it has been experimentally shown that asphaltene colloids in petroleum disperse systems may be transformed to long-lived (up to 6 months at RT) metastable states merely by a mild thermal pretreatment (e.g. 0.5 hr at 28-36°C). These states are fairly well-defined as revealed by distinctly different data sets for various parameters in non-treated (equilibrium) and pre-treated (metastable) fluids. In particular, at 20°C a metastable state is distinguished by $\approx 25\%$ increase of the mass of deposits at metal surfaces, by $\approx 5\%$ decrease of dynamic viscosity, etc. A plausible mechanism of transition to a metastable state is partial “desorption” of resin “shells” from asphaltene molecular nanoclusters (MNCs) as a result of a structural transformation of MNCs at $\approx 28^\circ\text{C}$. Consequently, steric stabilization of asphaltene colloids by resins is disrupted and directly interacting MNCs may form more complex aggregates, fairly long-lived at lower temperatures.

INTRODUCTION

Over the past years it has been recognised (e.g., Syunyaev et al, 1991) that a typical petroleum fluid is a hybrid of a solution and a colloidal dispersion (of crystallizing waxes, self-associating asphaltenes, etc.). Hence, understanding the phase behaviour of a complex petroleum disperse system should be expected to be a challenge. The surprise is that relatively simple (although, possibly, “unconventional”) experiments can shed light on details of phase transformations in such systems.

E.g., for long time a commonly accepted view in petroleum science has been that asphaltene molecules start to form colloidal particles (“micelles”, “aggregates”, “agglomerates”) only at concentrations above a “CMC” of about several grams per litre (Andersen and Christensen, 2000; Sheu, 1996). However, our recent measurements of optical absorptivities in “unconventional” highly diluted toluene solutions of oils and of solid asphaltene monomers apparently begins at concentrations not exceeding 1-2 mg/l, while massive aggregation of asphaltene occurs at 60-100 mg/l (cf. Fig.1). These results have been further supported by our measurements of refraction indexes and of dielectric constants in crudes of different origin (submitted for publication). An independent confirmation of asphaltene aggregation at 50-75 mg/l has been recently obtained in absorbance/fluorescence experiments (Goncalves et al., 2004). Moreover, our studies of viscosity and NMR relaxation in dilute solutions (Evdokimov et al., 2003c) indicated that the phenomenon of asphaltene aggregation at ≈ 100 mg/l may be described as a liquid-liquid phase separation (demixing transition), a conclusion recently supported by other authors (Sirota, 2004).

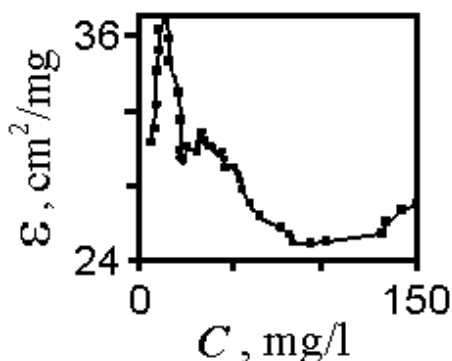


Fig. 1. Optical absorptivity ϵ of asphaltene at 540 nm as a function of asphaltene concentration C in crude oil/toluene solutions (adapted from Evdokimov et al., 2003c).

Other common concepts are that at concentrations, typical for natural petroleum systems: 1) the structure of asphaltene dispersion is fairly insensitive to small variations of ambient conditions, and 2) the state of asphaltene is thermodynamically controlled. Hence,

usually it is implicitly assumed that far from obvious critical/transition points the properties of asphaltene colloids are slowly varying smooth functions of external conditions, e.g. of temperature. Consequently, in a lot of conventional experiments temperature dependencies are investigated with fairly large intervals between consecutive data points, e.g. 15-40°C (Wong and Yen, 2000); 10-20°C (Priyanto et al., 2001) etc. Over the past several years we have conducted a series of rheological experiments with “unconventionally” small temperature increments of 1-2°C (Evdokimov et al, 2001;2003d;2004). Unexpectedly, we have observed reproducible non-monotonous temperature dependencies of some rheological parameters at temperatures of 10-50°C. These results were interpreted as an evidence of noticeable structural transformations in asphaltene colloids, induced by comparatively small temperature variations. These new states of asphaltenes may become long-lived metastable ones at lower temperatures (or long-lived transient ones due to a strong kinetic control of thermally-induced transformations of asphaltenes). Whatever the explanation, these experiments have shown that the current properties of an asphaltene-containing fluid may strongly depend on its thermal history. E.g., Fig. 2 shows that a low-temperature association energy of asphaltene particles in a model crude remains at a level of 8-11 kcal/mol (presumably characteristic of an “equilibrium” state of asphaltene colloids), in case the fluid previously has never been pre-heated at temperatures above 27-28°C. Thermal pre-treatment at temperatures 28-45°C evidently strongly transforms the structures and interaction energies of asphaltene particles – at low temperatures a new metastable (transient) state of asphaltene colloids is characterised by association energy of 32-34 kcal/mol. A plausible mechanism of transition to a metastable state is formation of more complex asphaltene associates, as confirmed by direct measurements by other authors (cf. Fig. 3).

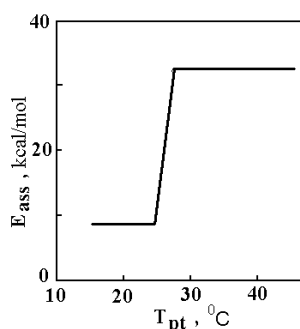
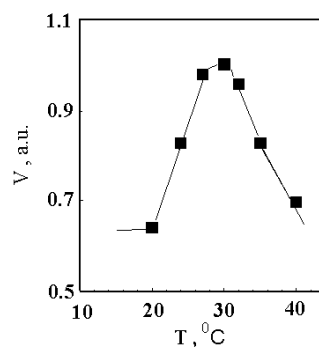


Fig. 2. Schematic behaviour of asphaltene association energies at 8-18°C E_{ass} , after 1 hr thermal pre-treatment at T_{pt} of a model crude oil with asphaltene concentration of 40 g/l (adapted from Evdokimov et al., 2001).

Fig. 3. Effects of temperature on the volume of asphaltene colloid particles in a model crude with asphaltene concentration of 36 g/l. (Fluorescence measurements of Dr. R.Z. Syunyaev, adapted from Evdokimov et al., 2001).



In the present communication we report the results of new experiments in support of thermally induced metastable (transient) states in asphaltene-rich fluids. Some preliminary data has been reported at the HOD-2004 conference (Evdokimov, 2004).

EXPERIMENTAL

Samples.

Experiments have been carried out with asphaltene-rich model oil (asphaltene concentration 12.3 g/l). The light hydrocarbon fractions were represented by toluene, the heavy oil fractions - by 11.6 wt. % of a vacuum residue from Western Siberian crudes (density at 20⁰C - 979 kg/m³ ; pour point - 18⁰C; boiling point - 342⁰C; asphaltenes - 10.9 wt. %). The components were mixed at room temperature 1 month before the experiments and were stored at RT (18-20⁰C) in a dark glass vessel, in air.

Measurements of heavy organic deposition were performed at metal substrates – two 1 mm thick steel plates with the total surface area of 256.1 cm³.

Apparatus and Procedure.

Deposition studies were conducted in a temperature controlled ($\pm 0.1^{\circ}\text{C}$) glass cell with steel substrates vertically immersed into the model oil, to minimise sedimentation effects. The mass of deposits was determined with an analytical balance (100 g capacity, 0.1 mg precision). Oil viscosities were measured in a temperature controlled Hoppler-type viscometer.

Between deposition/viscosity experiments, the model oil was stored at RT (18-20⁰C). Each individual experiment commenced with pre-heating the entire quantity of the model oil to the required measurement temperature for 15-20 minutes. Afterwards several ml of the liquid were transferred either to the deposition cell or to the viscometer. A standard deposition time was 20 minutes. Steel samples covered with deposits were dried in warm air and weighted. Before a new experiment the samples were washed in toluene, wiped with a cotton cloth and dried in warm air. This procedure restored the mass of steel plates to within 1 mg of its initial value.

It should be noted, that we had no strict scenario for choosing the individual measurement temperatures (i.e. no prescribed “descending order” or “ascending order”). To improve statistics, each next temperature was set virtually at random in the range of 11-40⁰C. Hence, in continuing experiments, the state of our model oil acquired more and more complicated thermal history.

RESULTS AND DISCUSSION

Deposition Data

The results of a series of deposition experiments are shown in Fig. 4.

Open squares denote the data set for an “equilibrium” state of the model oil, which in its thermal history has never been heated above 28°C (cf. Introduction). The apparent property of an “equilibrium” state (1) is an increase in the mass of deposits with increasing temperature up to ≈20°C, followed by a decrease of M at higher T .

Filled circles in Fig. 3 denote the data for the model oil with thermal histories including a structural transition at ≈28°C. A new state of the oil, induced by this transition, is distinguished by a notable increase in the mass of deposits at any measurement’s temperature (e.g. ≈25% at 20°C). A prevailing tendency in this state (2) is a continuing increase of deposits with increasing temperature. The thermally transformed oil is apparently in an “equilibrium” state (energetically preferable one) at 28-40°C, while below 28°C this state should be regarded as a metastable (transient) one.

The month-long experiments have shown that the discussed metastable state is fairly long-lived. E.g., in measurements at 17-27°C we never observed a relaxation of the oil to the low-temperature “equilibrium” state (denoted as “1” in Fig.4). In measurements at 11-16°C such relaxation occurred only in 40% of samples (cf. the respective bifurcation of data points in Fig.4). Moreover, at 20°C we have tested the thermally transformed model oil after six months storage at RT (18-20°C) and still observed a mass of deposits characteristic for a metastable (transient) state.

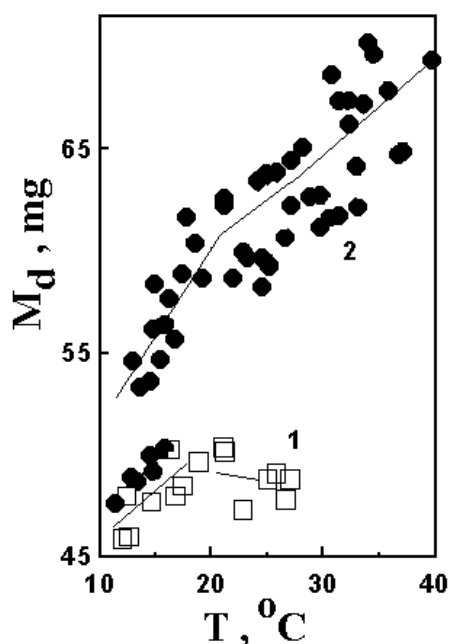


Fig. 4. Effects of deposition temperature and of the thermal history of asphaltene-rich model oil on the mass of deposits at steel samples. Open squares – data for the oil never heated above 28°C. Filled circles - data for the oil at least once pre-heated to 28°C, or to higher temperatures (note bifurcation of low-temperature deposits in this data set).

Viscosity Data

Some of the deposition experiments have been supplemented by measurements of viscosity in the model oil with the same thermal history. The results are presented in Fig. 5. Open squares and filled circles denote the same data as in Fig. 4. In this case a metastable (transient) state in oil, subjected to pre-heating above 28°C is distinguished by a persistent decrease of dynamic viscosity. In viscosity measurements we have never observed relaxation of the oil from a metastable state (2) to a low temperature “equilibrium” state (2), probably due to a comparatively smaller number of experiments.

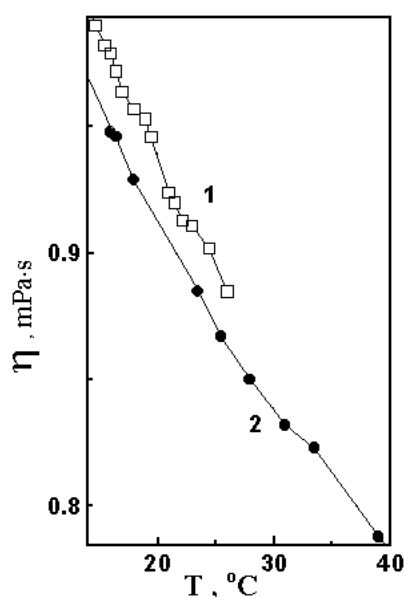


Fig. 5. Effects of deposition temperature and of the thermal history of asphaltene-rich model oil on its dynamic viscosity. Open squares – data for the oil never heated above 28°C. Filled circles - data for the oil at least once pre-heated to 28°C, or to higher temperatures.

Discussion

In accordance with our previous results (cf. Introduction), a plausible conclusion is that the observed transformations of the state of the studied multicomponent model oil are governed by equilibrium-metastable transitions in asphaltene colloids.

A schematic description may be that at $\approx 28^\circ\text{C}$ a structural transformation occurs in basic “molecular nanoclusters” (MNCs) of asphaltenes. As a result, MNC-MNC interactions become somewhat stronger, while interactions of MNCs with solvent molecules become somewhat weaker. Consequently, steric stabilization of asphaltene colloids by resins is disrupted and directly interacting MNCs may form more complex aggregates, fairly long-lived at lower temperatures.

For a given concentration (volume fraction) of asphaltenes, formation of complex deformable aggregates may indeed result in a lower viscosity, as follows from rheological theories for suspensions of deformable particles (e.g. Brenner, 1975; Manga et al., 1998, and references therein). This viscosity decrease by itself may facilitate a transport of depositing

material to a metal surface and may be responsible (at least partially) for the observed increase in the mass of deposits from the oil in a metastable (transient) state. Another reason for increased deposition may be the presumed higher activity of structurally transformed asphaltene MNCs.

Literature analysis has revealed some experimental results by other authors in favour of our basic assumption that the observed specific temperature of $\approx 28^\circ\text{C}$ is singled out by the processes involving solely asphaltenes and not other constituents of our multicomponent model oil. It should be emphasised that in respective publications the existence of this specific temperature remained unnoticed by the authors.

E.g. Ramos et al., 2001 measured viscosities and surface tensions as functions of concentration of pure C5I and C7I asphaltenes in various solvents. The inflections on concentration dependencies they ascribed to a “critical micelle concentration” (CMC) and to a “second aggregation concentration” (SAC). In Tables 1,2 of their paper the authors report the values of CMC and CAS at various temperatures, but do not plot the respective temperature dependencies. In Fig. 6 we show such a plot for toluene solutions of asphaltenes where the temperatures in the vicinity of 28°C are clearly singled out indisputably due to some physicochemical processes involving asphaltenes.

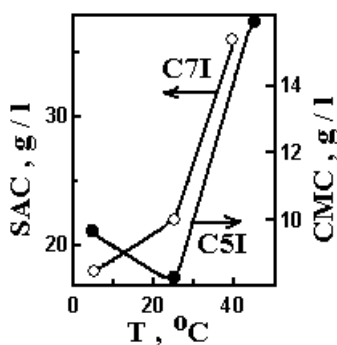


Fig. 6. Non-monotonous temperature dependencies of critical aggregation concentrations of asphaltenes in toluene (adapted from Ramos et al., 2001).

CONCLUSIONS

Measurements of various properties of asphaltene-containing fluids indicate the existence of a specific temperature close to 28°C , apparently singled out by some noticeable transformation of asphaltene colloids. The transformed structures are evidently equilibrium above 28°C and are quenched to a long-lived (up to six months) metastable (transient) state at lower temperatures. This state may be easily resolved from the corresponding equilibrium one by a well-defined difference in the values of the liquid's bulk properties.

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