

THERMALLY-INDUCED VISCOSITY ANOMALIES IN EMULSIONS UTILISED IN OIL RECOVERY OPERATIONS

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Introduction.

The factors contributing to the rheological parameters and to the colloid structure of petroleum emulsions is a problem of great concern and economic importance to the development of oil reservoirs. Crude oils are mostly invariably accompanied by water. Water-in-crude oil emulsions are usually produced by the shear action and the pressure gradient drop in the well-head chokes and valves and in the production pipelines. Bitumen emulsions are injected into oil reservoirs to increase recovery efficiency. There is a high industrial demand for viscosity data for petroleum emulsions, particularly for those with very heavy oil components, rich in resins and asphaltenes. Still, only a limited number of results are available on emulsion viscosities as detailed functions of such important external parameter as temperature. Moreover, the determination of the inner structure of emulsions via the majority of structure-sensitive measurements is only possible when the fluid is at rest. In contrast, rheometrical measurements offer means to evaluate the inner structure of emulsions in course of their flow.

Recently [1-3], we have shown that the rheological parameters of some petroleum fluids are sensitive to such subtle structural transformations, which often can not to be detected by other experimental techniques. Hence, in this study we regarded a viscometer as a probe not only of the macroscopic flow parameters but also of the microscopic features of the molecular-structure in petroleum emulsions

Samples and Experimental Methods.

The crude oil/water samples (25 vol.% of the emulsified reservoir water) were obtained directly from the oil-production well (Romashkinskoje reservoir, Tatarstan). The water-free oil phase contained 3.5 wt.% asphaltenes, 1.6 wt.% waxes, 22 wt.% resins. During prolonged laboratory storage at room temperature, oil and water phases separated from the samples by gravity, so that the studied W/O emulsions were formed again by intensive mixing of the separated phases.

The bitumen emulsions were formed from the "HIMEKO" concentrate (HIMEKO Co., Moscow) which contains 50 vol.% of bitumen, 40 vol.% of water and 10 vol. % of stabiliser (CaCl_2), acid (HCl), various surfactants, dispersants and modifiers. According to the technological recommendations of by the producer, the final bitumen emulsions were formed by 1/1 dilution of the concentrate with the separately provided "KORE" solvent (hydrocarbon rectification residues).

The effect of formation temperature on rheology of all samples have been investigated at flow temperatures of 8°C - 30°C , for shear rates up to 150 s^{-1} , in a Brookfield Programmable DV-II+ Viscometer (Brookfield Eng. Labs., Inc., USA), equipped with a

YULA-15 Adapter with a concentric cylinder geometry. The inner cylinder diameter was 25.15 mm with the gaps of 1.23 mm. Each rheological experiment has been performed with a new, freshly-prepared sample.

In studies of water/oil emulsions (25 vol.% of reservoir water), two gravitationally separated phases were mixed again directly in the rheometer's measurement cell. The bitumen concentrates also were diluted in the rheometer's cell by adding an equal volume of industrial dilutant so that a studied emulsions contained 25 vol.% of bitumen and 20 vol.% of water. Each emulsion was formed by mixing for 1 hour at conditions close to a maximum rheometer's torque (shear stresses $\approx 0.7-0.8 \text{ N/m}^2$), at a fixed formation temperature TF in the range from 20°C to 60°C. After formation was completed, each sample under constant mixing was cooled at the rate of 1-1,5°C per minute to the lowest measurement (flow) temperature of 8-10°C.

At each operating temperature, the system was initially maintained at a constant shear rate for 20 min. The measurements continued with a step-like decrease of the shear rate down to 0.1-0.2 s⁻¹. At each shear rate the torque and shear stress data were collected for 90-120 s and averaged. Before changing to the next measurement (flow) temperature (in 2°C steps, up to 30°C), the shear rate was increased to its initial value. With the above procedure, the typical duration of one experiment was about 6 hours.

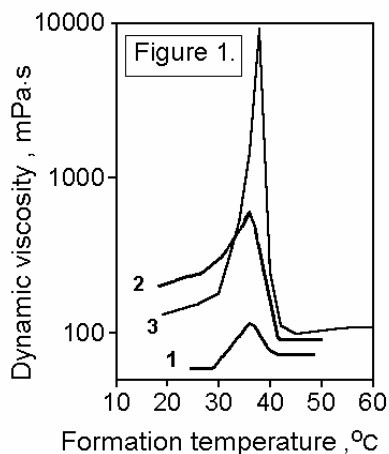
In all studied samples non-Newtonian flow behaviour was observed at shear stresses below 0.2-0.5 Pa. Hence, to characterise the temperature-induced effects, we have used the viscosity values at shear stress of 0.7 Pa, i.e. at flow conditions close to Newtonian.

Experimental results.

1. The effect of the formation temperature on the viscosity of emulsions.

It was observed, that viscosities of emulsions, measured at industrially-important flow temperatures 10-28°C is strongly affected by their formation temperature TF. Figure 1 shows the effect of TF on the dynamic viscosity for (1) the bitumen emulsions, at 16°C; (2) the water/crude oil emulsions, at 12°C; (3) the water-free oil phase of the W/O emulsions, at 12°C. Note, that the viscosity values are plotted on a log-scale. As can be seen in Figure 1, in all samples even relatively small variations of the formation temperature may lead to very large changes of dynamic viscosity, measured at lower temperatures. All results show a technologically unfavourable sharp increase of viscosity for the "critical" formation temperatures of 36-38°C. For example, the viscosity of the water-free oil, pre-heated to these temperatures, increases by a factor of 70, to 9070 mPa·s, as compared to 129 mPa·s, measured for unheated oil, stored at 19°C. In the water/oil emulsions the corresponding viscosity increase is somewhat lower – from 200 mPa·s to 600 mPa·s. Obviously, the thermal effects in water/oil emulsions should be attributed to its oil component. A smaller effect of heating for water/oil emulsions, as compared to the original crude may be explained by the fact that the viscosity of the mineralised reservoir water, contained in such emulsion, did not show any viscosity anomalies in the studied temperature range. The results of Figure 1 show that unfavourable increase of viscosity after formation at "critical" temperatures is also observed in bitumen emulsions. The reason why this increase is only two-fold (from 60 to 120 mPa·s) may be due to a presence of specially introduced surfactants/stabilisers, as discussed above.

The data of Figure 1 reveal the small width of the “critical range” of formation temperatures, leading to the observed unfavorable thermal effects. At the FWHM of the crude oil viscosity peak, this TF range may be determined as 2,2⁰C. The most conservative estimates at the base of the viscosity peak give for the critical TF range the value not exceeding 10⁰C.

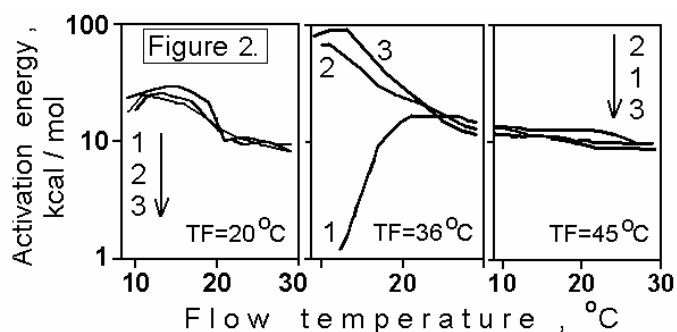


In course of all experiments, the results of the thermal treatment (modified viscosities) were still detected even after prolonged (up to 6 hours) annealing at increasing flow temperatures in conditions of a continuing mechanical agitation.

This indicates that some long-lived extended molecular structures appeared in the emulsions after the fabrication processes at “critical” temperatures (the effect of long-term “thermal memory”). In the matrix crude oil phase, this “thermal memory” was found to extend for a period of at least four months.

2. Activation energies of the viscous flow.

Activation energies were determined from the dependencies of the logarithm of viscosity on the reciprocal flow temperature, by fitting straight line approximations (the Arrhenius plots) between the consecutive experimental points. To reduce a random scatter, the obtained sets of activation energies were smoothed with a three-point sliding data window. The results of these calculations are presented in Figure 2 for (1) the bitumen emulsions; (2) the water/crude oil emulsions; (3) the water-free crude oil.



The left part of Figure 2 shows the dependencies of activation energies on the flow (measurement) temperature for samples, subjected to room temperature formation (TF=20⁰C). The notable feature is a virtual coincidence of activation energies for all studied samples. For flow temperatures decreasing from

30⁰C down to 20⁰C all activation energies remain fairly constant, slowly increasing within the limits of 8.5-10.5 kcal/mol (\approx 36-44 kJ/mol). At temperatures close to 20⁰C there is a step-like increase of the activation energies to a new level of 22-29 kcal/mol (\approx 92-121 kJ/mol). Below 10-12⁰C the activation energies show the tendency of decreasing, so the shape of the curves in the range of 8-20⁰C may be described as a “flat maximum”.

The right part of Figure 2 shows the results for TF=45⁰C, above the critical formation temperatures. The effects of such a strong pre-heating are rather small. For all flow temperatures the activation energies are reduced approximately to the level, observed at 20-30⁰C in case formation at TF=20⁰C.

The most pronounced changes of activation energies were registered (central part of Figure 2) after formation of emulsions at $TF=36^{\circ}C$, close to the critical temperature in the matrix crude oil. In this case activation energies for the W/O emulsion and the crude sharply increase from 10-12 kcal/mol (42-50 kJ/mol) to 70-100 kcal/mol (290-420 kJ/mol) with flow temperatures decreasing from $30^{\circ}C$ to $10-12^{\circ}C$. In contrast, activation energies for bitumen emulsion sharply decrease at low flow temperatures, down to 1.5 kcal/mol (6.3 kJ/mol) at $13^{\circ}C$. The observed large variations of activation energies are indicative of notable modifications of the emulsion' molecular structures induced by formation in the critical TF range. These structural modifications we attribute primarily to the specific molecular processes involving asphaltenes.

Discussion.

It is known that asphaltenes may stabilise water (oil) droplets in emulsions formed by recovery of crudes [4-7] and in bitumen emulsions [8,9]. It is mostly the aggregation state of the asphaltenes and not their amount that controls the stability of an emulsion. When asphaltenes start to form large aggregates, their impact on emulsion stability is the greatest [10,11]. Accordingly, when the asphaltene particles/aggregates are dissolved to substantially smaller units, they no longer produce stabilising effects.

Based on these results, it can be concluded that the asphaltene fractions, are primarily responsible for the stability of the emulsion's inner structure. The degree of asphaltene aggregation determines the strength of this structure. Hence the observed sharp variations of viscosity may be attributed to some specific aggregation processes involving asphaltene molecules.

Asphaltene colloids are known to be sterically stabilised by solvated resins [13]. Formation of larger asphaltene aggregates may occur when resin molecules "desorb" from the surfaces of asphaltenes. The sharp dependence of the measured viscosities on the value of TF (Figure 1) suggests that the changes in solvation is triggered by a structural phase transition in the asphaltene/resin molecular subsystem. In [2,3] we discussed two possible types of these transitions at temperatures just above $30^{\circ}C$. One is a first-order transition between closely packed and loosely bound structures in the adsorbed layers of resin molecules. Another possible mechanism is the change of the surface energy of the asphaltene aggregates due to phase transformation of their inner molecular structure.

An important role in the observed thermal effects is evidently played by paraffins. It has been repeatedly shown [6,7,12] that the paraffins alone are unable to stabilise petroleum emulsions. In the absence of asphaltenes, paraffin crystals remain completely oil-wet (hydrophobic) and are dispersed in the oil phase. However, when asphaltene aggregates adsorb on the surfaces of paraffin particles, their wettability changes. The asphaltene-solvated paraffin particles migrate to the oil-water interface, contributing to the formation of rigid layers around water droplet and to the emulsion stability [6,7].

Types of paraffin fractions may determine the role of paraffins in the observed thermal effects in petroleum emulsions. The studied crude oils contained predominantly normal paraffins with the melting points of $40-50^{\circ}C$. Bitumen are known to contain also the microcrystalline paraffins (isoparaffin and cycloparaffin) with higher melting points of $60-90^{\circ}C$.

During a sufficiently strong pre-heating (TF above both the asphaltene/resin phase transition and the melting point of paraffins) all the existing paraffin particles melt away. The new microscopic crystals start appearing in the emulsion only when it is cooled below the melting point. We presume, that large asphaltene aggregates can not form an “adsorbed layer” around a small paraffin crystal. Hence, with decreasing temperature, the newly-formed paraffin crystals form networks, directly interacting with each other. Direct interaction of paraffins is a weak physical one [12], so that the resulting increase of viscosity is comparatively small and such loosely-bound crystal networks quickly disappear when the temperature is increased again.

During a moderate pre-heating (TF below the melting point of paraffins, but above the asphaltene/resin phase transition) the existing paraffin particles in emulsions readily adsorb the newly-formed asphaltene aggregates, so that their interaction properties of these particles are notably altered. After cooling, asphaltene-covered paraffin particles form strongly bound networks, so that the viscosity is greatly increased and “memory” of the pre-heating parameters is preserved at varying measurement conditions.

The relatively smaller thermal effects in the bitumen emulsions may be due to the weakening of asphaltene-mediated networks by other strong surfactants introduced into the concentrated product.

The means by which asphaltenes, resins and paraffins interact in petroleum fluids remains the subject of speculation but association by hydrogen bonding and by formation of charge-transfer π - π complexes have been cited as the causative mechanisms [13]. Through these noncovalent interactions, asphaltene molecules may influence the structure of emulsions by forming a mechanical barrier around the water droplets [14].

The strength of intermolecular bonds of asphaltenes may be evaluated from the changes in activation energies of the viscous flow, as shown by viscosity studies in solutions, containing coal asphaltenes [15]. The removal of hydrogen bonds and of π interactions decreased activation energies by 33 kJ/mol and by 30 kJ/mol, respectively. These results were verified by IR-spectroscopy [16], which showed that energies of hydrogen bonds were on average 30-50 kJ/mol (for some individual bonds up to 70 kJ/mol).

Our measurements after formation at 20 °C (Figure 2) show a step-like decrease of activation energies by 50-60 kJ/mol for flow temperatures exceeding 20°C. This decrease may be attributed to a (reversible) thermally-induced break-up of intermolecular hydrogen and/or π -bonds in the asphaltene subsystems. Accordingly, an overall decrease of activation energies after the strong pre-heating (TF=45°C, Figure 2) should be due to an irreversible removal of these noncovalent bonds.

Finally, formation of emulsions in the “critical” temperature range (TF=36°C, Figure 2) induces the structural changes, characterised by a large increase of activation energies of up to 300-380 kJ/mol, indicative of a possible covalent bonding. Namely, this increase is close to the energies (\approx 380-420 kJ/mol) of unactivated CH and CC bonds in organic compounds.

Conclusions.

We found that formation temperature of emulsions has a very strong impact on viscosity of crude oil and bitumen emulsions. At normal technological conditions these emulsions possess a long-term “memory” of a thermal preheating. This memory is especially strong after formation of emulsions at “critical” temperatures of about 36-38⁰C. The “critical” sharp increase of the technological viscosity is attributed to structural phase transitions in asphaltene molecular aggregates. In W/O emulsions and in the crude oil these aggregates presumably stabilise the extended networks of paraffin particles by emerging covalent bonding. The relative weakening of the inner structures in bitumen emulsions may be due to the presence of producer-added surfactants. In all studied emulsions, the “memory” of a strong pre-heating (formation temperatures above the melting point of paraffins) may be explained by destruction of noncovalent hydrogen bonds and π -interactions.

This study demonstrates the effectiveness of rheological measurements as a means to elucidate the inner structures of petroleum and bitumen emulsions over a wide range of temperatures. With this paper we hope to stimulate further research work on thermodynamics and mechanics of asphaltene-containing emulsions utilised in recovery of oil reservoirs.

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