

PECULIARITIES OF RHEOLOGY OF CRUDE OIL AND BITUMEN EMULSIONS AT INDUSTRIALLY IMPORTANT TEMPERATURES

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1. Introduction

The factors contributing to the rheological and structural parameters of petroleum emulsions is a problem of great concern and economic importance to the oil companies in the production of oil from underground reservoirs. Water-in-crude oil emulsions are usually produced at 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/structural data for such emulsions, particularly for those with heavy oil components, rich in resins and asphaltenes. The inner structure of emulsions is determined via the majority of structure-sensitive measurements only when the fluid is at rest. In contrast, rheometrical measurements offer an indirect means to study the structure of flowing emulsions.

Recently, we have shown that the rheology of petroleum fluids is highly sensitive to structural transformations in the asphaltene-resin subsystems (1,2). Hence, in this study we regard a viscometer as a probe not only of the flow parameters but also of the molecular structure of petroleum emulsions.

2. Materials and Methods

2.1. Samples

The water/crude oil samples (25 vol.% of the emulsified reservoir water) were obtained directly from the oil-production well (Tatarstan, Russia). The 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 by gravity, so that the studied W/O emulsions were prepared by re-mixing the separated phases at the initial v/v ratio.

The bitumen emulsions were prepared from the "HIMEKO" concentrate (HIMEKO Co., Moscow) which contains 50 vol.% of bitumen (pavement grade), 40 vol.% of water and 10 vol.% of stabiliser (CaCl₂), acid (HCl), various unspecified surfactants, dispersants and modifiers. As recommended by the producer, industrial bitumen emulsions are prepared by 1/1 dilution of the concentrate with the separately provided "KORE" solvent (hydrocarbon rectification residues). Both products were used as received.

2.2 Apparatus and procedure

The effect of formation temperature on rheology of all samples have been investigated at flow temperatures of 8⁰C-30⁰C, 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 (a concentric cylinder geometry). Each rheological experiment has been performed with a freshly prepared sample.

In studies of W/O emulsions, two gravitationally separated phases were introduced into the rheometer's cell at the volume ratio of 1/3, equal to that in the production well (25% v/v of water). The bitumen concentrates were diluted in the rheometer's cell by adding an equal volume of industrial dilutant so that emulsions contained 25% v/v of bitumen and 20% v/v of water. Each emulsion was mixed for 1 hour at a maximum rheometer's torque (shear stresses ≈0.7-0.8 N/m²), at a fixed formation temperature TF in the range from 19⁰C to 60⁰C. Under constant mixing, each sample was cooled to the lowest operating (flow) temperature (8-10⁰C) at the rate of 1-1,5⁰C per minute.

At each operating temperature, the system was initially maintained at a constant shear rate for 20 min. The tests began at the highest shear rate and measurements continued at shear rates decreasing 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 operating temperature (in 2^oC steps, up to 30^oC), the shear rate was increased to its initial value. With the above procedure, the typical duration of one experiment was about 6 hours.

3. Results

3.1. Shear stress dependencies of viscosity

For all studied samples the measured flow curves (viscosity vs. shear stress) exhibited a shear-thinning (i.e. non-Newtonian) behaviour. In case of W/O emulsions and the matrix crude oil, the flow curves became close to Newtonian at shear stresses ≥ 0.15 -0.4 Pa, depending on the formation and the flow temperatures. For bitumen emulsions, the Newtonian approximation could be applied only at higher shear stresses, above 0.6 Pa.

As a measure of temperature-induced effects in all samples, we have used the viscosity value at a common shear stress of 0.7 Pa, i.e. at flow conditions closest to Newtonian.

3.2. Constant-shear viscosities before after thermal preload

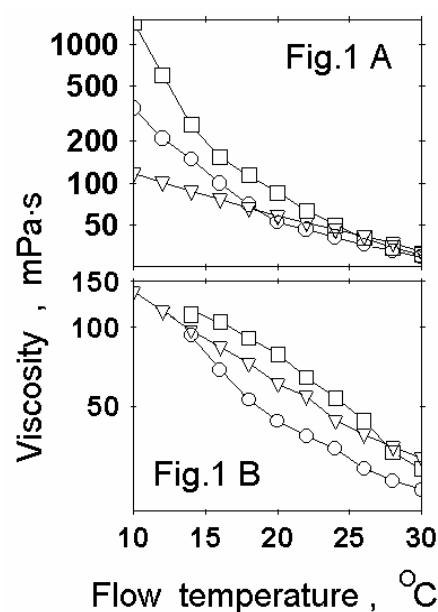
The viscosity of the emulsions was strongly affected by their fabrication temperature TF.

Fig.1(A,B) shows the effect of TF on the dependencies of viscosity at a constant shear stress (0.7 N/m²) on the flow (measurement) temperature, for the W/O emulsions (A) and for the bitumen emulsions (B). Note the log scale for viscosities. The data denoted by circles were obtained after fabrication at room temperature (TF=24^oC), without thermal preload. Squares and triangles denote the results for TF=36^oC and TF=45^oC, respectively. In all cases the viscosity decreases with increasing flow temperature due to the enhanced thermal mobility in the samples. However, the rate of this decrease (as well as the viscosity value at any flow temperature) shows a strong non-monotonic dependence on the fabrication temperature.

For the water-crude oil emulsions (Fig.1 A), a moderate thermal preload (TF=36^oC) leads to a large increase of viscosities as compared to emulsions, fabricated at room temperature. At flow temperature of 10^oC this increase is from 372 mPa·s to 1440 mPa·s.

A stronger thermal preload (TF=45^oC) causes a qualitatively opposite effect of decreasing the viscosities as compared to the RT data. At flow temperature of 10^oC the decrease is from 372 mPa·s to 116 mPa·s. For W/O emulsions the effects of the thermal preload are largest at low flow temperatures and are gradually levelled off as the flow temperature is increased up to 30^oC. Qualitatively similar (but much stronger) effects were observed also for the matrix crude oil (cf. Figs.2,3).

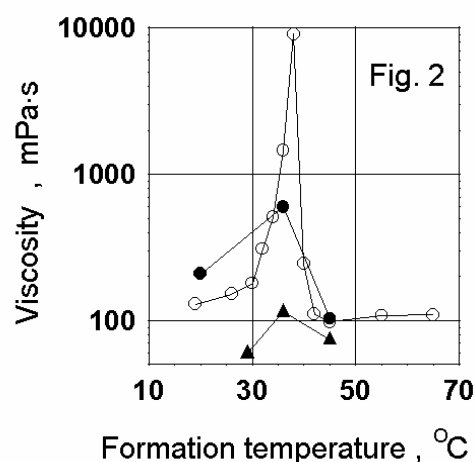
For the bitumen emulsions (Fig.1 B) a moderate thermal preload (TF=36^oC) also leads to the viscosity increase, but only at flow temperatures above 13-14^oC. At flow temperature of 16^oC the viscosity increases from 61 mPa·s (RT fabrication) to 115 mPa·s. However, below 13^oC there is an apparent reversal of the TF effect – viscosity values for TF=36^oC show a tendency to be lower than those for TF=24^oC. A higher thermal preload (TF=45^oC), leads to a general decrease of measured viscosities but, as distinct from crude oil emulsions, these viscosities remain larger than those measured after RT formation.



3.3. The critical formation temperatures and the effect of thermal memory

As follows from the previous section, small variations of the thermal preload (formation temperature) may lead to quantitatively large and even qualitatively different changes of viscosity, measured at lower temperatures in petroleum emulsions. In order to determine the role of oil emulsion constituents in this effect, we made similar rheological measurements with the separated phases. The viscosity of the reservoir water did not show any peculiarities in the studied ranges of the formation/flow temperatures. The viscosity of the matrix crude oil showed qualitatively the same effects of formation temperature, but much more pronounced than those in the studied emulsions, as illustrated in Fig.2.

Filled triangles in Fig.2 denote the viscosity values (measured at 16⁰C) for the bitumen emulsions prepared at different formation temperatures. Filled circles denote the analogous data for the crude oil emulsions (measured at 12⁰C). The results for the matrix crude oil (also measured at 12⁰C) are denoted by open circles and show a very sharp peak of viscosity for the “critical” formation temperature of 38⁰C. The peak viscosity value is 9070 mPa·s, as compared to 129 mPa·s, measured after room temperature (19⁰C) formation of the crude oil sample. The data of Fig.2 reveal the small width of the “critical range” of formation temperatures, leading to the observed thermal effects.



At the FWHM of the crude oil viscosity peak, this “critical range” of TF 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.

...The results of Fig.2 definitely prove that the observed effects of a thermal preload in the W/O emulsions are related mainly to the changes in the properties of the matrix crude oil. The considerably smaller effect in the bitumen emulsions may be due to a presence of specially introduced surfactants/stabilisers, as discussed in section 4.3.

...In course of all experiments, the results of the thermal preloads (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 residual structures remained in the emulsions after the fabrication processes at “critical” temperatures (the effect of long-term “thermal memory”). In the matrix crude oil, this “thermal memory” was found to extend for a period of at least four months, as revealed by viscosity measurements after storage at room temperatures.

3.4. 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 Fig.3 A,B,C, where the thick solid lines are the data for W/O emulsions, thin solid lines – the data for the matrix crude oil and the dashed lines - the data for bitumen emulsions (note the log scale for activation energies).

Fig.3A shows the dependencies of activation energies on the flow (measurement) temperature for samples, subjected to room temperature formation (20⁰C for W/O emulsion and the matrix crude oil, 26⁰C for bitumen emulsions). The notable feature of Fig.3A is a virtual coincidence of activation energies for all studied samples.

For flow temperatures decreasing from 30⁰C down to about 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”.

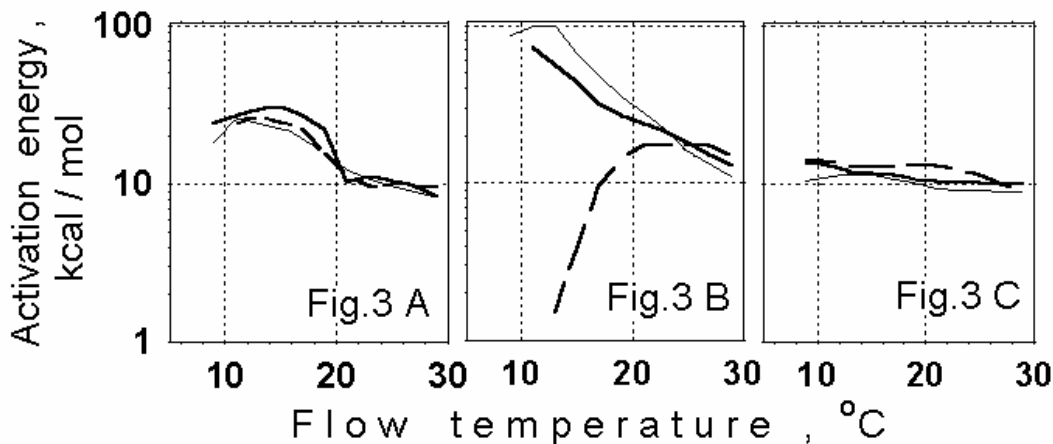


Fig.3C show the results for TF=45⁰C, i.e. above the critical formation temperatures. The effects of such a strong thermal preload are rather small. For all flow temperatures the activation energies are reduced approximately to the level, observed at 20-30⁰C in case of RT formation (Fig.3A).

The most pronounced changes of activation energies are seen (Fig.3B) after formation of emulsions at TF=36⁰C, 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 30⁰C to 10-12⁰C. In contrast, activation energies for bitumen emulsion sharply decrease at low flow temperatures, down to 1.5 kcal/mol (6.3 kJ/mol) at 13⁰C. The observed large variations of activation energies are indicative of notable modifications of the emulsion structures induced by formation in the critical TF range. These structural modifications we attribute to the specific molecular processes involving asphaltenes.

4. Discussion

4.1 The role of asphaltenes

It is a well-known fact that the presence of asphaltene fractions serves to stabilise the emulsions formed during crude oil production (3-6) and that asphaltenes also play a dominant role in the stabilisation of water droplets in diluted bitumen emulsions (7,8).

It is mostly the aggregation state of the asphaltenes and not their amount that controls the structure of an emulsion. When asphaltenes start to form large aggregates, their impact on emulsion properties is the greatest (9,10). For example, it was observed (8) that in diluted bitumen emulsions (8) the emulsified water droplets are stabilised by steric repulsion between adsorbed “monolayers” (8-10 nm thick) of asphaltene aggregates on the droplet surfaces. Similarly, it was concluded from rheological measurements of asphaltene-containing crude oil - water emulsions (9), that the water droplets are stabilised by adsorbed 10 nm asphaltene layers, consistent with the size of asphaltene aggregates. Accordingly, when the asphaltene particles/aggregates are dissolved to substantially smaller units, they no longer produce stabilising effects.

Based on the above arguments, it can be concluded that the asphaltene aggregates, when present, are primarily responsible for the strength of the emulsion's structure. Hence the observed sharp variations of viscosity may be attributed to some specific aggregation processes involving asphaltene molecules.

4.2. The “trigger” mechanism of asphaltene aggregation after thermal preload

Asphaltene colloids are known to be sterically stabilised by solvated resins (12). Formation of larger asphaltene aggregates may occur when resin molecules are “desorbed” from asphaltenes. The sharp dependence of the measured viscosities on the value of TF (Fig.2) suggests that the changes in solvation is triggered by a structural phase transition in the asphaltene/resin subsystem. In (1,2) we discussed two possible types of these transitions at temperatures just above 30⁰C. One is a first-order transition between closely packed and loosely bound structures in the adsorbed layers of resin molecules. Another possible “trigger mechanism” is the change of the surface energy of the π -stacked asphaltene aggregates due to phase transformation of their inner molecular structure.

4.3. The role of waxes

It has been proved (5,6,11) that the wax fractions alone do not to stabilise petroleum emulsions. In the absence of asphaltenes, wax crystals are oil-wet and are dispersed in the oil phase. However, when asphaltene aggregates adsorb on the wax particles, their wettability changes from complete oil-wetting to a mixed (intermediate) wetting, which allows the wax crystals to have affinity to the aqueous phase. The asphaltene-solvated wax particles migrate to the oil–water interface, contributing to the formation of rigid layers around water droplet and to the emulsion tightness (5,6).

Types of wax crystals and their thermal properties determine, how wax could interfere with the thermally-induced effects in petroleum emulsions. The studied crude oils contained predominantly normal paraffin waxes with the melting points in the range of 40–50⁰C. Bitumen are known to contain also the microcrystalline (isoparaffin and cycloparaffin) waxes with higher melting points, in the range of 60–90⁰C.

During a strong thermal preload (TF above both the asphaltene/resin phase transition and the wax melting point) all wax particles melt away. The new microscopic wax 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” at small wax crystals. Besides, above the phase transition point, asphaltenes may become wax inhibitors, because large aggregates no longer serve as crystallisation centres. With decreasing temperature, the newly-formed wax crystals form networks by weak physical direct interactions (11), so that the resulting increase of viscosity is small and such loosely-bound crystal networks quickly disappear when the temperature is increased again.

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

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

4.4 Interpretation of the activation energies

The means by which asphaltenes, resins and waxes interact to exist in petroleum 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 (12).

Through these noncovalent interactions, asphaltene molecules may influence the structure of emulsions by forming a mechanical barrier around the water droplets (13). The strength of interactions may be evaluated from the changes in activation energies of the viscous flow. The removal (by chemical additives) of hydrogen bonds and of π interactions in coal solutions decreases activation energies by 33 kJ/mol and by 30 kJ/mol, respectively (14). These results are close to the bond strengths in coal solutions directly determined by IR-spectroscopy (15). The IR average strengths of hydrogen bonds were 30-50 kJ/mol, while some individual bonds had the strengths of up to 70 kJ/mol.

...Our measurements after RT formation (Fig.3A) show a step-like decrease of activation energies by 50-60 kJ/mol for flow temperatures exceeding 20°C. In view of the above results, this decrease may be attributed to a (reversible) thermally-induced break-up of intermolecular hydrogen and/or π -bonds in the asphaltene subsystems of the studied emulsions. Accordingly, an overall decrease of activation energies after the strong thermal preload (TF=45°C, Fig.3C) should be due to an irreversible removal of noncovalent bonds present in the RT-formed samples.

...Finally, formation of emulsions in the “critical” temperature range (TF=36°C, Fig.3B) 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, the least reactive parts of organic compounds.

5. Conclusions

We found that formation temperature has a very strong impact on viscosity of crude oil and bitumen emulsions, characterised by a long-term memory of a thermal preload. This memory is especially strong after formation at “critical” temperatures of about 36-38°C when the sharp increase of viscosity is attributed to structural phase transitions in asphaltene molecular aggregates. In W/O emulsions and in the matrix crude oil these aggregates may stabilise the extended networks of wax particles by emerging covalent bonding. The “memory” of a stronger thermal preload (at temperatures above the wax melting point) may be due to destruction of noncovalent hydrogen and π -bonds.

This study demonstrates the effectiveness of rheological measurements as a means to indirectly 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 dynamics of asphaltene-containing emulsions.

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