Colloid Polym Sci 277:41–47 (1999)

ORIGINAL CONTRIBUTION

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Effect of alkaline materials on interfacial rheological properties of oil-water systems

Received: 6 April 1998
Accepted: 18 August 1998

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Abstract Interfacial rheological properties of a model crude oil-water system were studied in the presence of sodium hydroxide. The interfacial viscosity, the non-Newtonian flow behavior and the activation energy of viscous flow were determined as a function of shear rate, alkali concentration and aging time. The fundamental conclusion of the experimental results is that the interfacial viscosity drastically decreases in the presence of alkaline materials and the change under favorable conditions may exceed 3 or 4 orders of magnitude. Simultaneously, the sodium hydroxide effectively suppresses the non-Newtonian flow behavior of the interfacial layer. The experimental observations are explained by simultaneous chemical processes taking place in the boundary layer. The present data may help to elucidate the formation, stability and breaking of alkali-containing oil-water emulsions and they provide additional information for better understanding of the displacement mechanism and for the formulation of alkaline flooding as a potential chemically enhanced oil-recovery method.

Key words Alkaline materials – Interfacial rheology – Oil-water interface – Rigid films

Introduction

Although the idea of alkaline flooding in enhanced oil recovery (EOR) came up more than 70 years ago, it was taken into account as a realistic alternative only in the 1970s. Despite this fact, fundamental consideration of the method has changed only a little in the past few years. Namely, the improved recovery factor in the presence of alkalis is still attributed to interfacial tension lowering [1], wettability alteration [2], elimination of rigid films at oil-water interfaces [3], initiation phase inversion in dispersed systems [4] and, finally, precipitation of multivalent cations from the formation water which may also influence the ion-exchange processes in the reservoir [5]. Thus, the effect of alkalis can be explained by "oil-alkali" and "alkali-rock" interactions; however, any or all of these mechanisms can operate in a particular operation and consequently EOR pilot tends to be site-specific in terms of process design and dominant recovery mechanism.

In the case of alkaline flooding numerous alkaline compounds were tested. The efforts were mostly focused on sodium hydroxide, sodium carbonate, sodium orthosilicate or their mixtures. Since the chemical interaction between specific native components and the alkalis was considered to be one of the most important questions, detailed laboratory studies also concentrated on correlation of the phase properties with the interfacial effect. In a rating survey by Smith [6] it was stated that oils with significant amounts of vacuum distillate have high probabilities of exhibiting alkaline reactivity. Others made more precise statements on the nature of chemical interactions. A generally accepted conclusion is that the crude oil must contain acidic components which react with the alkaline materials in the interface. The "soaps" formed under normal conditions might then decrease the interfacial tension by several orders of magnitude [1], implying that a loose, but definitive correlation exists between the interfacial-tension lowering and the acid number of oils. On the other hand, the positive effect significantly depends on the preadsorption mechanism of naturally occurring surfactants present in oils [7]. Similarly, deZabala et al. [8] emphasized that a high acid number is necessary but is not the only precondition for efficient interfacial-tension lowering, because not all the hydrolyzed organic precursors are interfacially active.

These observations have been well-known for some time, though the phenomena were detailed with respect to interfacial rheological properties in only a few papers. The role of interfacial viscosity in displacement processes using alkaline materials [9, 10] has recently been called to our attention. Wasan and coworkers [11, 12] and Neustadter et al. [13] reported that coalescence of oil droplets and formation of oil banks (preconditions for efficient oil displacement) might be expected only if low interfacial tension is accompanied by similarly low interfacial viscosity. Encouraged by these data it seemed necessary to study the interfacial rheological properties of different Hungarian oil-water systems and to determine the effect of some EOR chemicals thereon [14–16]. On the basis of previous studies the following conclusions were drawn.

1. The viscosity of interfacial layers may change within extremely wide limits (10^{-2}–10^{4} mNs/m) and non-Newtonian flow behavior is general for all systems.
2. The viscosity usually increases and the non-Newtonian flow behavior strengthens with time; however, the time dependency of the interfacial rheological properties significantly depends on the type of crude oil.
3. The interfacial rheological properties depend considerably on the quality of the aqueous phase. In the presence of inorganic electrolytes the viscosity may decrease by an order of magnitude, while the basic non-Newtonian flow behavior usually remains unchanged.
4. The interfacial viscosity decreases with temperature. The dynamics of the change is influenced, however, by the shear rate and time. The activation energy of viscous flow decreases with increasing shear rate and decreasing aging time. This fact implies that a relatively thick interfacial layer forms at rest, which can be disintegrated only by high shear forces.
5. The interfacial viscosity, the non-Newtonian flow behavior and the activation energy of the viscous flow drastically decrease in the presence of non-ionic surfactants: modification of these interfacial properties increases with decreasing ethoxy group number.

The earlier studies have also shown that all interfacial rheological properties are individual factors which might be used for identification and characterization of different oil-water systems (reservoirs and even wells). In order to enhance our knowledge of crude oil-water interfaces, laboratory studies were extended to the analysis of the effect of alkaline materials. The present results are evaluated with respect to the role of the interfacial rheological properties in oil field (EOR/IOR) chemistry.

Experimental

The measurements were carried out with a Contraves low shear 30 rotational viscometer using a biconical bob. The flow curves were recorded between 10^{-3} and 10^{2} s^{-1} shear rates applying a linear rate program and a 2 min ramp time. The interfacial properties were determined in the temperature range 303–333 K. The activation energy of the viscous flow was calculated from the temperature dependence of the viscosity at different shear rates using the de-Guzman relationship. The maximum aging time of phases was 24 h. A characteristic Hungarian crude oil (Battonya Ba-55) served as a model in order to demonstrate the effect of alkaline material on interfacial rheological properties. The origin and some physical and chemical properties of the oil are listed in Table 1. According to earlier studies, the Ba-55 oil-water system represents an average behavior with respect to both the absolute interfacial viscosity and its shear rate dependency. Before the rheological measurements were made the oil was dewatered by centrifugation and passed through a column filled with $CaCl_2$. Analytical grade alkaline materials, particularly NaOH were used as additives in the concentration range 0–5 g/l.

Results and discussion

Reisberg and Doscher [3], and Bourgoyne et al. [17] have shown that irreversible rigid films, which may strongly

Table 1 Origin and properties of the Ba-55 oil used as a model

Character	paraffinic
Formation depth (m)	950–995
Age of reservoir	lower Pliocene
Density[a] (g cm)	0.80
Viscosity[b] (mPa s)	3.80
Temperature (K)	338
Atmospheric distillate (%)	33.00
Vacuum distillate (%)	57.00
Distillate residue (%)	8.40
Asphaltene content (%)	1.1
Resin content (%)	0.2
Formation water	chloride type
Salt content (g/l)	16.5 (80% NaCl)

[a] At 298 K
[b] At 303 K

influence the coalescence of dispersed droplets in a continuous phase, form at crude oil-water interfaces. The chemical driving force behind this phenomena is the free energy of the system which diminishes considerably on formation of monomolecular films, rigid membranes, etc., if native components of the oil phase are enriched in the boundary layer. Owing to the composition of crude oils, the interfacial layer is generally of composite character and, in many cases, a penetrated film containing solid asphaltene particles is formed. Obviously, this third phase differs from the bulk phases not only in chemical composition, but also in rheological properties. On the other hand, the high viscosity of the hydrocarbon phases usually makes diffusion a decisive factor in the formation of a boundary layer. Consequently, the interfacial rheological properties may show simultaneously both time- and temperature-dependent features.

Although the problem of interfacial rheology was summarized in the excellent monographs by Joly [18, 19], the correct theoretical treatment of our experimental results was difficult, because the crude oil-water systems are multicomponent. Thus, we must be content mostly with the empirical description of phenomena, investigating those factors which may influence the interfacial rheological properties in the presence of NaOH.

Effect of type and concentration of alkalis

In the first test series the effect of different alkaline materials was determined. The measurements were carried out at a concentration of 0.5 g/l at 303 K. Hydroxides and carbonates were used as models and the curves in Fig. 1 correspond to 4 h contact time. The experimental data allow the following general conclusions to be drawn.

1. The interfacial viscosity decreases in all cases; however, there are great differences among the alkaline materials. The relative effects follow the order: $NaOH > KOH > Na_2CO_3 > K_2CO_3$.
2. Non-Newtonian flow behavior is characteristic in all cases, but the least shear rate dependency of the interfacial viscosity is observed when NaOH is present in the aqueous phase.
3. At high shear rates (greater than 0.1 s^{-1}) the effect of alkaline materials is negligible, viz. the effect of alkaline materials on interfacial rheological properties is predominant in the low shear-rate range where the structure of the boundary layer is determined by weak molecular interactions.

As a next step the effect of concentration was determined. The measurements were carried out in a concentration range of 0–5 g/l at 303 K. The basic interfacial properties of the model Ba-55 oil/distilled water system are illustrated in Fig. 2, where the interfacial viscosity is plotted as a function of shear rate and time. As shown, the viscosity belonging to short lifetimes of the interface is less than 0.1 mNs/m and it depends only slightly on shear rate, while the viscosity increases gradually by several orders of magnitude and the structural viscosity becomes predominant with time. The results imply that when evaluating the effect of NaOH the contact time is a crucial factor and it fundamentally modifies the basis of comparison.

The above statement is seen to be true from the response surfaces shown in Figs. 3 and 4. The data correspond to aging times of 0 and 4 h and allow the following conclusions to be drawn.

1. The most obvious effect of NaOH is that the interfacial viscosity drastically decreases even in the case when the NaOH content is merely 0.1 g/l. At zero aging time the effect is not striking, but at 4 h

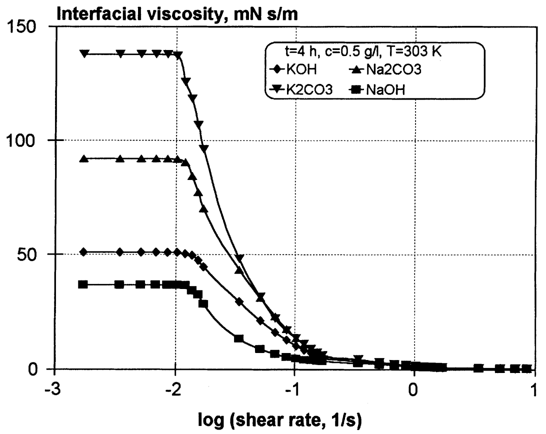

Fig. 1 Effect of different alkaline materials on interfacial viscosity (Ba-55 oil, $T = 303$ K)

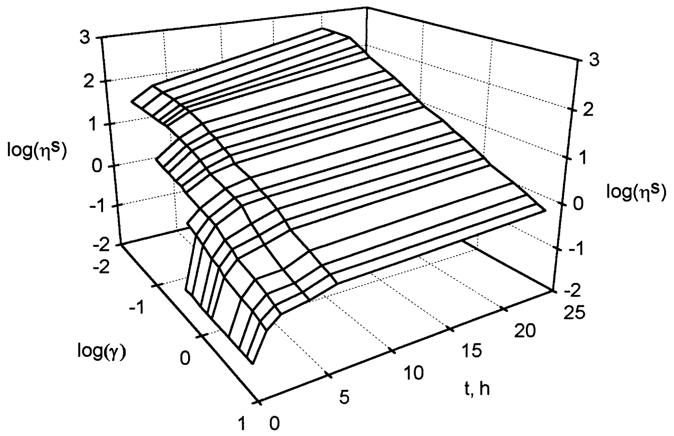

Fig. 2 Dependence of interfacial viscosity on shear rate and aging time in a Ba-55 oil/distilled water system ($T = 303$ K)

the change exceeds 3 orders of magnitude depending on the shear rate.

2. The positive effect increases with NaOH concentration, but the change reaches an equilibrium above 1 g/l. This critical value can be rendered to termination or completing of the chemical reactions taking place in the interfacial layer which lead to formation of active surfactants in the boundary layer.
3. NaOH effectively suppresses the non-Newtonian flow behavior. At short aging time elimination of the structural character is absolute, while in case of aged interfacial films the shear-dependent viscosity is uniformly characteristic, but the extent of the non-Newtonian feature is much less than in case of alkali-free systems (Figs. 3, 4).

Simultaneous processes are responsible for the complex phenomena. The instantaneous effect might be attributed to the simple impact of inorganic salts on interfacial rheological properties [14]. As demonstrated earlier for different crude oil-water systems, monovalent cations (e.g. NaCl) may decrease the interfacial viscosity by an order of magnitude, depressing the dissociation equilibrium of the acid-type organic compounds enriched in the boundary layer. Posthydrolysis as a chemical reaction is then superimposed on the size and conformational modification of the adsorbed molecules. Since the latter is a time-dependent process, the interfacial rheological properties become sensitive to both the concentration of NaOH and the aging time.

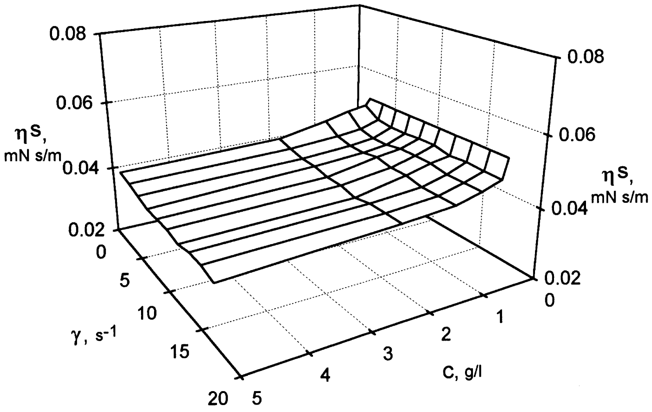

Fig. 3 Dependence of interfacial viscosity on shear rate and NaOH concentration (Ba-55 oil, $t = 0$ h, $T = 303$ K)

Effect of temperature

The analysis of temperature might be important because the viscosities of homogeneous liquids decrease exponentially with temperature (de-Guzman equation), the inter- and intramolecular interaction in rigid films may change significantly at elevated temperature and at last, but not least, the kinetics of the chemical reaction between the preadsorbed compounds with NaOH is also temperature dependent (Arrhenius equation). Therefore, a detailed test program was carried out with the aim of elucidating the effect of temperature. Some representative results which were obtained at NaOH concentrations of 0.5 and 5.0 g/l are shown in Figs. 5 and 6. Using all the data available at different temperatures the following conclusions could be drawn.

1. The relative effect of temperature depends on NaOH concentration. The curves in Fig. 5 clearly show that interfacial viscosity decreases with temperature and the change hardly depends on shear rate. At high NaOH concentration temperature has only a negligible impact on interfacial viscosity, but apparently the relative change in the low shear-rate region is slightly greater than at high shear rates.
2. As mentioned in the previous section, the non-Newtonian character of the curves is not remarkable

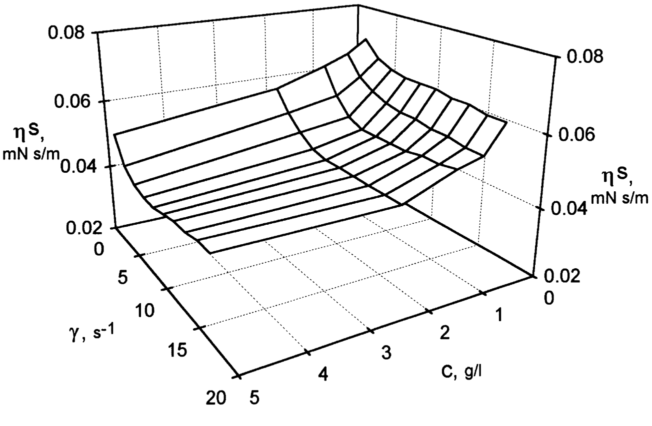

Fig. 4 Dependence of interfacial viscosity on shear rate and NaOH concentration (Ba-55 oil, $t = 4$ h, $T = 303$ K)

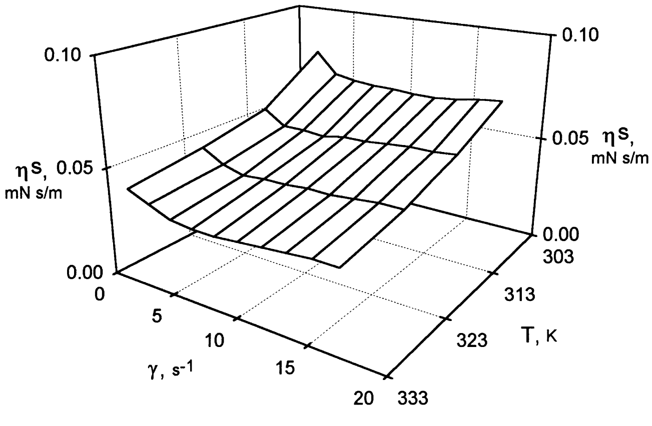

Fig. 5 Dependence of interfacial viscosity on shear rate and temperature (Ba-55 oil, $t = 4$ h, $c_{\mathrm{NaOH}} = 0.5$ g/l)

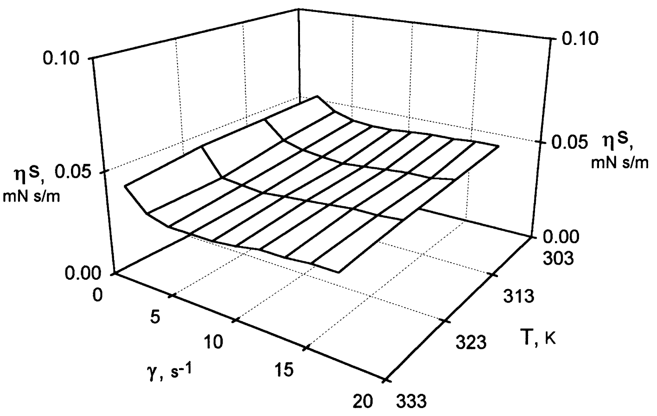

Fig. 6 Dependence of interfacial viscosity on shear rate and temperature (Ba-55 oil, $t = 4$ h, $c_{\mathrm{NaOH}} = 5.0$ g/l)

for systems containing alkaline material, but it still exists at all temperatures and concentrations. Despite this fact the remaining structural effect increases at elevated temperature.

3. The negligible effect of shear rate found in the presence of NaOH changes only a little with temperature. This observation indirectly proves that the original "rigid" film characteristic in oil/distilled water systems is transformed to a "liquid" interface. It is also interesting that at high temperature and in an equilibrium state the structure of the interfacial layer is similar and is independent of the original alkali concentration.

Chemical reactions (posthydrolysis, soap formation, etc.) should be considered as major factors determining the interfacial properties of alkali-containing oil-water systems. At high temperatures these reactions are fast and, therefore, the final rheological consequences are hardly influenced by the aging time and, above all, by the alkali content of the aqueous solution.

Effect of aging time

Theoretically, the dynamics of the change in the interfacial rheological properties is jointly temperature and concentration-dependent. Since the reaction rate is simultaneously influenced by both factors, it was expected that the interfacial viscosity would be highly dependent on aging time. Some remarks made in previous sections show that this is far from being true in most cases. Taking the experimental results obtained for pure oil/distilled water systems and basic reaction kinetics considerations into account, this fact might be confusing. The curves in Fig. 7 definitely show that in the early time periods of an interface, between 0 and 1 h, the interfacial rheological properties change steeply because of the relatively slow rate of chemical reactions.

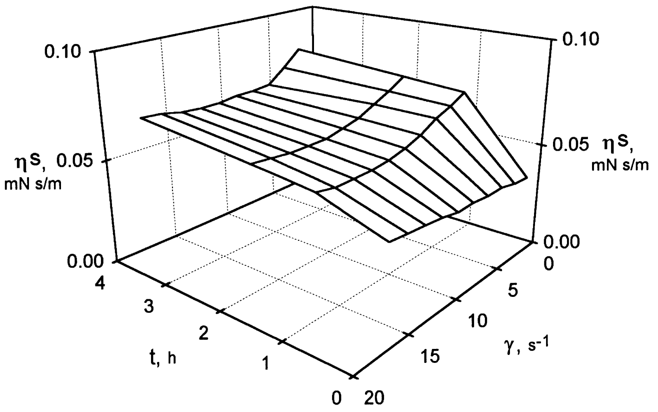

Fig. 7 Dependence of interfacial viscosity on shear rate and aging time (Ba-55 oil, $T = 303$ K, $c_{\mathrm{NaOH}} = 0.5$ g/l)

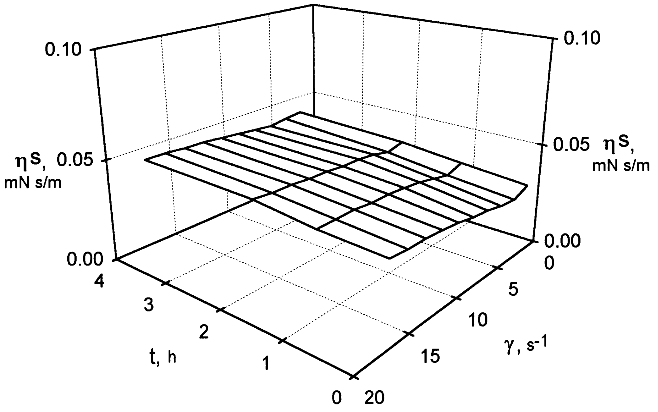

Fig. 8 Dependence of interfacial viscosity on shear rate and aging time (Ba-55 oil, $T = 303$ K, $c_{\mathrm{NaOH}} = 5.0$ g/l)

In contrast, at high alkali concentration (5 g/l, Fig. 8), such an upward section on the response surface is completely absent because the reaction in the interface takes place within seconds. (In this context it must be mentioned that the zero aging time often referred to in this paper is actually the first possible measuring point which belongs to 1–3 min lifetime of the fluids in contact. This unfavorable limitation is of a technical nature.)

Activation energy of the viscous flow in the presence of NaOH

Calculation of the activation energy of viscous flow (Gibbs energy according to Eyring's theory) provided additional arguments to the previous statements. The ΔG^* value was determined by the temperature dependency of the interfacial viscosities in the range 303–333 K. Independent variables were the shear rate, NaOH concentration and the aging time. According to the "hole" concept, the activation energy represents the energy consumption or dissipation needed to propagate the "flow unit", viz. to maintain the irreversible deformation in liquids. For the Ba-55 oil/distilled water system the calculated ΔG^* values obtained in the same temperature range were between 10 and 60 kJ/mol and show strong shear-rate and aging-time dependency [16]. In the presence of NaOH the systematic analysis revealed the following features.

1. The activation energy of viscous flow in NaOH containing oil-water systems is usually less than 10 kJ/mol and it practically does not depend on shear rate.
2. The effect of alkali concentration on ΔG^* is characteristic only in the range 0–1 g/l (Figs. 9, 10).
3. The aging time has a measurable impact on the activation energy, particularly at low NaOH concentrations. For instance, at long aging time and low NaOH content the maximum ΔG^* values measured were 15–18 kJ/mol.
4. The activation energy characteristics above 1 g/l NaOH content are in the same range as calculated for systems containing nonionic surfactants with short ethoxy chain lengths [16]. Despite this fact the properties and structure of the interfacial layer must be different, because quite different chemical and physical processes are responsible for interfacial viscosity lowering.

The phenomena mentioned above can be attributed to structural changes of the interfacial layer. At rest, the characteristically high (> 50 kJ/mol) and shear-dependent activation energy suggests that part of the energy is consumed by the elastic deformation of the structure, by disintegration of the intermolecular network and, accordingly, by the large flow units existing in alkali-free systems [16]. When NaOH is added to the aqueous phase, much weaker chemical forces characterize the interaction of the structure-forming molecules, the size and volume of the flow unit decrease and, hence, the activation energy also decreases and it becomes independent of the shear rate. Since the phenomena are closely connected with the chemical reactions taking place in the interfacial layer, the rising tendency of ΔG^* observed in the concentration range 0–1 g/l NaOH is entirely reasonable.

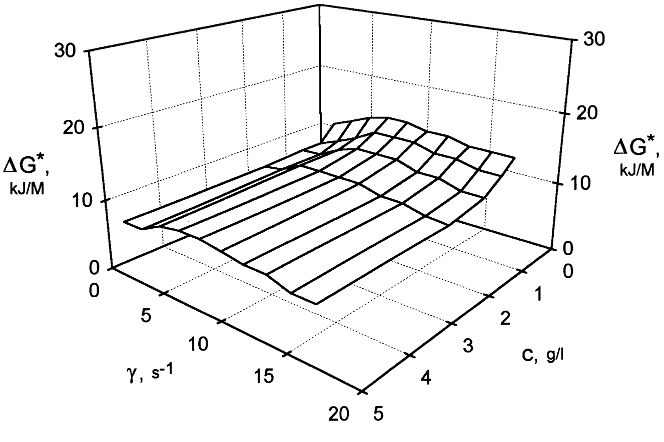

Fig. 9 Dependence of the activation energy of the viscous flow on shear rate and NaOH concentration (Ba-55 oil, t = 0 h)

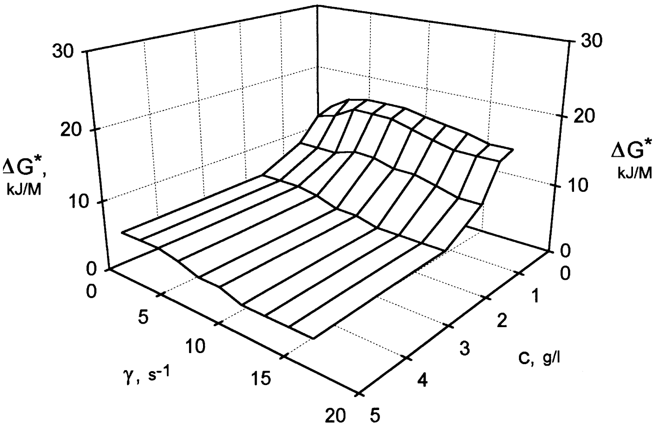

Fig. 10 Dependence of the activation energy of the viscous flow on shear rate and NaOH concentration (Ba-55 oil, t = 4 h)

As was pointed out in a previous paper [16], the absolute ΔG^* value and its change under experimental, industrial, etc., circumstances may serve as a reliable basis for prediction of emulsion stability or of the propensity and rate of coalescence. Consequently, the activation energy might be accepted as a quantitative measure of the processes mentioned. According to this approach the high activation energy renders a stable emulsion hard to break, while activation energies less than 10 kJ/mol imply that the immiscible phases emulsify readily, but they also break rapidly at rest if other stabilizing factors (e.g. presence of asphaltene, clay, etc., particles) have only negligible impact on the whole process. The experimental results are in full agreement with those observations reported in the literature [11–13] and the present calculation of the activation energy may also provide an energetic interpretation of those findings.

Conclusions

Interfacial rheological properties of a model crude oil-water system in the presence of NaOH were studied and the following conclusions were drawn.

1. The interfacial viscosity drastically decreases in the presence of alkaline materials and the change under

favorable conditions may exceed 3 or 4 orders of magnitude. The greatest effect was observed in the presence of NaOH.

2. The positive effect of alkaline materials depends slightly on concentration, but an equilibrium or constant value of interfacial viscosity is always reached above 1 g/l. Simultaneously, the alkalis, particularly NaOH effectively suppress the non-Newtonian flow behavior of the interfacial layer.

3. Although the interfacial viscosity gradually decreases with temperature, the change hardly depends on shear rate; namely, a residual non-Newtonian flow behavior remains a characteristic of the interface.

4. The activation energy of viscous flow in NaOH containing oil-water systems is usually less than 10 kJ/mol and this value is similar to those calculated for surfactant-containing systems.

5. The effect of independent variables (shear rate and temperature) on interfacial rheological properties increases with aging time, but substantial influence was tested only at low NaOH concentrations.

The experimental observations are explained by simultaneous processes taking place in the boundary layer. Chemical reactions (hydrolysis, soap formation, etc.) between the preadsorbed natural amphipatic compounds and NaOH are considered to be the major factors, but modification of the dissociation equilibrium of organic acids leading to size and conformation changes is also proposed. The present data may help to elucidate the formation, stability and breaking of oil-water emulsions and they provide additional information for a better understanding of the displacement mechanism and for the formulation of alkaline flooding as a potential chemically enhanced oil-recovery method.

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