057 ROLE OF INTERFACIAL RHEOLOGICAL PROPERTIES OF OIL/WATER SYSTEMS IN MECHANISM AND DESIGN OF EOR/IOR TECHNOLOGIES

JULIANNA LAKATOS-SZABÓ¹, ISTVÁN LAKATOS¹, and BÉLA KOSZTIN²
¹ Hungarian Academy of Sciences, Research Laboratory for Mining Chemistry,
PO Box 2, 3515 Miskolc-Egyetemváros, Hungary
² MOL Plc.

Abstract

Interfacial rheological properties of different Hungarian crude oil/water systems were determined in wide temperature and shear rate range and in the presence of inorganic electrolytes, tensides, alkaline materials and polymers. The detailed laboratory study definitely proved that the interfacial rheological properties are extremely sensitive parameters towards the chemical composition of immiscible liquids. Therefore, comparison and interpretation of the interfacial rheological properties may contribute significantly to extension of the spectrum of the reservoir characterization, better understanding of the displacement mechanism, development of more profitable EOR/IOR methods, intensification of the surface technologies, optimization of the pipe line transportation and improvement of the refinery operations.

Introduction

The secondary and tertiary recovery processes, particularly the chemical floodings, are based on influencing the interfacial properties in a favourable direction. It is curious, however, that the interfacial rheological properties are absolutely neglected as part of the capillary phenomena. The absurdity of this understanding is even more obvious if we consider that Reisberg and Doscher [1], and Bourgoyne et al. [2] have already shown many years before that irreversible rigid films may form at crude oil/water interfaces, which can strongly influence spontaneous sorption or displacement processes and some papers were also published recently, in which the authors emphatically called attention to the role of interfacial viscosity in the displacement mechanism [3,4]. A decade ago Wasan et al. [5,6], and Neustadter et al. [7] proved that spontaneous demulsification of emulsions, coalescence of particles and formation of a so-called oil bank, which is the precondition of an efficient oil displacement, might be expected only if a low interfacial tension is accompanied by a similarly low interfacial viscosity.

Taking this data into account, it seemed necessary to investigate the interfacial rheological properties of different Hungarian oil/water systems. As a first step, the fundamental interfacial rheological properties of crude oils with different composition and origin were determined against different aqueous phases were determined. Later the laboratory studies were extended to determine the effect of different chemicals (inorganic salts, tensides, alkaline materials and polymers) on interfacial rheological properties.

Experimental conditions

The measurements were carried out with Contraves Low Shear 30 rotational viscometer using a bi-conical bob. The flow curves were recorded between 10^{-3} and 10^2 s^{-1} shear rate using linear rate program and 2 min ramp time. The interfacial properties were determined in temperature range of 303-343 K. Activation energy of the viscous flow was calculated by the temperature dependence of viscosity obtained at the same shear rate. The maximum ageing (contact) time of phases was 24 h. Comparison was also made among oil/water systems using constant shear rate. Characteristic Hungarian crude oils were used as a model in order to demonstrate the great variety of interfacial rheological properties. Analytical grade

chemicals were applied to study their effect on interfacial rheological properties of a representative oil/water system.

Results and Discussion

1. Characterization of different crude oil/water systems

At the boundary of two immiscible liquids, the free energy of a system consisting of bulk phases and an interface between them, diminishes considerably on formation of monomolecular films, rigid membranes, etc., if distinguished components of oil are enriched in the boundary layer. It was already shown for oil-water systems in the beginning of the 1950's that natural surfactants become highly enriched in the interfacial layer, and their presence considerably diminishes interfacial tension. On the other hand many publications dealt also with the theoretical problems of surface and interfacial rheology, but they did not offer a practical possibility for the correct theoretical treatment of our experimental results, because the crude oil/water systems are multicomponent and owing to the composition of crude oils, the interfacial layers are generally of composite character penetrated by asphaltene particles. Thus, we mostly must be content with the empirical description of phenomena predicting that the interfacial rheological properties will show simultaneously time and temperature dependent features.

As the basic interfacial rheological property of different Hungarian crude oil/water systems are concerned it was definitely concluded that the interfacial rheological properties significantly depend on type of the crude oil (Fig. 1.), composition of the aqueous phase, ageing (contact) time of the interface and the temperature [8]. According to the general observations the interfacial viscosity and the deviation from the Newtonian behaviour significantly increase with the ageing time (Fig. 2.). The temperature dependence of the flow curves, and particularly the activation energy of the viscous flow, may serve as a reliable basis for quantitative prediction of the phase behaviour. Particularly the change of activation energy is noteworthy since it implies that in the initial period of the phase contact the low activation energy promotes the spontaneous emulsification, while at long ageing time its high values favour the stabilisation of the interface. The following interfacial rheological parameters can be used for characterization of a crude oil/water system: viscosity, non-Newtonian flow behaviour, time and temperature dependency of the rheological parameters, and activation energy of the viscous flow. The rheological models and their parameters describing the flow curves or the η - $\dot{\gamma}$ relationships provide further possibilities for quantitative characterization of the oil/water systems. Namely, the zero shear viscosity, rotation relaxation time, shear thinning index, etc. may improve drastically the reliability of differentiation among the two-phase systems having otherwise similar chemical, physical and bulk phase rheological properties. Since the listed parameters are individual and sensitive properties of a crude oil/water system, these factors may offer new tools for characterization and identification of the difference between the hydrocarbon reservoirs and the independent oil bearing layers (wells) even in the same reservoir.

2. Effect of non-ionic surfactants on interfacial rheological properties

The micellization of different ethoxylated nonyl-phenols has been discussed earlier in detail [9, 10]. Since the parameters characterizing the structure of micelles and the micellar solutions varied between wide limits, relatively great differences in interfacial rheological properties were expected among the systems containing the same tensides. The experimental results have completely met the expectation as shown in Figs 3-4. where the effect of ethoxylated nonyl-phenols ($n_{EO} = 10-40$) on interfacial viscosity is plotted as a function of shear rate at 303 and 333 K, respectively. The curves demonstrated here and the data published elsewhere [11-12] prove the following conclusions:

- a) The non-ionic tensides significantly reduce in interfacial viscosity, and the lower the ethoxy group number, the greater the viscosity reduction.
- b) The effect of tensides significantly increases with the concentration up to the c.m.c.
- c) The tensides highly influence the non-Newtonian flow behaviour. The slightly ethoxylated products have more positive effect than the tensides with long ethoxy chain and elimination of the structural viscosity is often followed, particularly at low ethoxylation, by dilatancy.
- d) The dependence on ageing time still exists in all cases, however, the set of equilibrium conditions generally requires less time. The process is the fastest at tensides with the shortest ethoxy chain.

The interfacial properties may be well correlated with the interfacial tenside concentration. According to the generally accepted concept the highest tenside concentration exists in the boundary layer when the tenside has limited solubility in both phases, viz. the partition coefficient is close to the unity. In the present case the surfactants with short ethoxy chain are predominantly oil-soluble, while the highly ethoxylated products are water-soluble. Consequently, the highest interfacial tenside concentration exist in the tested oil/tenside solution systems when $n_{EO}=8-10$, and that fact is converging with the experimental findings [12].

3. Effect of alkaline materials on interfacial rheological properties

The effect of alkaline materials on interfacial rheological properties of oil/water systems was studied first by Wasan et al. [5, 6]. Ample results were collected by the authors to conclude that the interfacial viscosity significantly decreases in presence of sodium hydroxide. The phenomenon was attributed to esterification and saponification of natural surfactants adsorbed at the interface from the oil phase. The results of the present investigation are parallel with those mentioned above. The Battonya crude oil used as model was tested against an aqueous phase containing sodium hydroxide in concentrations between 0.1 and 10.0 g/l and in temperature range of 303-333 K. The general observations can be summarised as follows:

- a) In presence of alkaline materials the interfacial viscosity may decrease by orders of magnitude and the average values are usually less than 0.1 mNs/m (Fig. 5.).
- b) The alkaline materials suppress the non-Newtonian flow behaviour: at short contact time the interfacial layers show practically Newtonian character.
- c) The viscosity decreasing effect and suppression of the structural viscosity increases with the concentration, but the radical effect ensues at a certain concentration, which is roughly 1 g/l. Probably, that critical value can be rendered to the initiation of the chemical reactions taking place in the interfacial layer leading to formation of more active "natural" surfactants (Fig. 6.).
- d) The effect of temperature on interfacial rheological properties is dominant only at low alkali concentrations and long contact times (Figs 5-6.).

The experimental findings suggest why the alkali-containing systems readily form emulsions often reported in alkaline flooding, which break rapidly. In these cases either the alkali concentration is too low (high alkali consumption in the reservoir) or the dynamic forces re-emulsify permanently the liquid system.

4. Effect of polymers on interfacial rheological properties

Unique colloid chemical processes might be observed in presence of macromolecular substances. For instance, formations of coarse dispersed systems hard to break were reported frequently in polymer pilots. Since the polymers are not prone to adsorb at water/oil interfaces, the plausible explanation must be sought in other directions. With the aim at elucidating the phenomena different polyacrylamides were added to the aqueous phase in concentration range of 0.1-2.0 g/l. Until now the following conclusions were drawn:

- 1) The polymers have substantial suppression effect in respect to both the viscosity and the non-Newtonian flow behaviour. The favourable effect is, however, far less than that of the surfactants.
- 2) The basic characteristics observed in oil/water systems free of any chemicals are pronounced only at low polymer concentration and in case of low molecular weight, unhydrolyzed polymers (Fig. 7.)
- 3) Using high molecular weight, partially hydrolyzed polymers and relatively high polymer concentration the rheological properties become invariant to ageing time, temperature and shear rate (Fig. 8.).

The experimental results obtained in the presence of polymers can be correlated with the solution structure. Strong dependence on experimental factors governs the interfacial processes when the polymer solution is still a particulate system, but over a critical polymer concentration, in "network" state, their effects on interfacial rheological properties become secondary.

Role of interfacial rheological properties in oil field chemistry

The great diversity and wide limits of interfacial rheological properties of natural crude oil/water systems may allow us to conclude that their impact on recovery processes and surface technologies are certainly crucial. Conclusive results were obtained to predict the following consequences:

Effect of high interfacial viscosity on subsurface processes:

- more displacing force (energy, pressure gradient, etc.) is required to maintain the constant flow rate;
- the smallest pores are plugged by the fragments of the rigid films,
- both the relative and the absolute permeability becomes worst;
- the residual oil saturation increases;
- the emulsion formed in-situ becomes more stable; and
- both the microscopic displacement and the volumetric sweep efficiency decrease.

Effect of high interfacial viscosity on surface processes:

- emulsions hard to break form in the surface facilities;
- chemical technology is needed to break the emulsions;
- optimisation of the chemical technology is difficult;
- much greater precision is required in the technological control;
- more labour skill is necessary;
- the environmental hazard of the surface technology and the transportation is increased; and
- sporadic and unpredictable problems may arise at the oil field and in the refineries.

Thus, an outstanding expertise in interfacial rheology is considered not only as desired but definitely needed in the tailoring and formulation of chemical technologies to be applied at oil fields.

Conclusions

A detailed laboratory study definitely proved that the interfacial rheological properties are extremely sensitive parameters towards the chemical composition of immiscible formation liquids. Therefore, comparison and interpretation of the interfacial rheological properties will probably contribute to extension of the weaponry of the reservoir characterisation, better understanding of the displacement mechanism, development of more profitable EOR/IOR methods, intensification of the surface technologies, optimisation of the pipe line transportation and improvement of the refinery operations.

The experimental observations and findings can also be generalised from a colloid chemical point of view. For instance it can firmly be stated that formation of emulsions is controlled primarily by the interfacial tension, while the coalescence of emulsion is controlled primarily by the interfacial viscosity. It was definitely shown that the interfacial rheology is an efficient and powerful detection technique, which may enhance our knowledge on formation, structure, properties and behaviour of interfacial layers. Thus, it will probably accelerate significantly the progress in all areas of colloid science and technology.

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Fig. 1. Dependence of the interfacial viscosity on shear rate (different Hungarian oil/dist. water)

Fig. 2. Dependence of the interfacial viscosity on contact (ageing) time (Ba-65 oil/dist. water)

Fig. 3. Effect of shear rate and ethoxy group number on interfacial viscosity of oil/tenside solution systems at 303 K temperature ($c_s=1$ g/l)

Fig. 4. Effect of shear rate and ethoxy group number on interfacial viscosity of oil/tenside solution systems at 333 K temperature ($c_s=1$ g/l)

Fig. 5. Effect of shear rate and temperature on interfacial viscosity in oil/alkaline solution systems ($c_{\text{NaOH}} = 0.5 \text{ g/l}$)

Fig. 6. Effect of shear rate and temperature on interfacial viscosity in oil/alkaline solution systems ($c_{\text{NaOH}} = 5.0 \text{ g/l}$)

Fig. 7. Effect of shear rate and temperature on interfacial viscosity in oil/polymer solution system ($c_{\text{NP-10}} = 1 \text{ g/l}$)

Fig. 8. Effect of shear rate and temperature on interfacial viscosity in oil/polymer solution system ($c_{\text{AP-30}} = 1 \text{ g/l}$)