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Effect of ethoxylated nonyl-phenols on interfacial rheological properties of oil/water systems

Received: 10 August 1996
Accepted: 29 November 1996

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Abstract Interfacial rheological properties of different Hungarian crude oil/water systems were determined in wide temperature and shear rate range and in presence of ethoxylated nonyl-phenols with ethoxy group number between 10 and 40. The fundamental conclusion of the experimental results is that the interfacial viscosity, the non-Newtonian flow behavior and the activation energy of the viscous flow drastically decrease in presence of non-ionic surfactants. Modification of these interfacial rheological properties increase with decreasing ethoxy group number and increasing tenside concentration and

temperature. The most radical change was observed in presence of NPEO₁₀. As a summary it was evidenced that the interfacial rheology is an efficient and powerful detection technique, which may enhance our knowledge on formation, structure, properties and behavior of interfacial layers formed in oil/water systems. Thus, similar studies will probably accelerate the progress significantly not only in oil recovery but also in all areas of colloid science and technology.

Key words Surfactants – non-ionic tensides – interfacial rheology – oil–water interface – rigid films

Introduction

The interfacial phenomena play a fundamental role in conventional and enhanced oil recovery (EOR) methods. Therefore, it seems a reservoir engineering absurdity that only the interfacial tension and the wettability are regarded as factors shaping the microscopic displacement efficiency, and the interfacial viscosity being another native interfacial property is totally neglected. That fact is even more curious because Reisberg and Doscher [1], and Bourgoyne et al. [2] have shown many years before that irreversible rigid films form at crude oil/water interfaces, which may strongly influence the coalescence of dispersed droplets in a continuous phase. Though these observations have been well-known for some time, the phenomena were not detailed despite the anomalies of flow mechanism often observed in presence of chemicals. In recent years,

however, valuable papers in which the authors emphatically called attention to the role of interfacial viscosity in displacement processes using alkaline materials were published [3, 4].

Another aspect of the present studies is that substantial amount of petroleum is produced as W/O emulsion. Among others, Strange and Talash [5], Whiteley and Ware [6], and Widmyer et al. [7] explained the low displacement efficiency by in situ emulsification and high stability of oil/water emulsions. Later, Wasan et al. [8, 9], and Neustadter et al. [10] proved that coalescence of particles and formation of oil banks (preconditions of efficient oil displacement) might be expected only if the low interfacial tension is accompanied by similarly low interfacial viscosity.

Considering this data it appeared necessary to investigate the interfacial rheological properties of different oil/water systems and to determine the effect of EOR

chemicals thereon. First, the fundamental interfacial rheological properties of crude oils having different composition and origin will be illustrated, then we will focus on the effect of ethoxylated nonyl-phenols on interfacial viscosity, non-Newtonian flow behavior and activation energy of the viscous flow. The results will be evaluated in respect to role of interfacial rheological properties in colloid and oil field chemistry.

Experimental conditions

The measurements were carried out with Contraves Low Shear 30 rotational viscometer (Couette measuring principle) and a biconical bob. The flow curves were recorded between 10^{-3} and 10^2 s^{-1} shear rates using linear rate program and 2 min ramp time. The interfacial properties were determined in the temperature range of 303–343 K. Activation energy of the viscous flow was calculated by temperature dependence of viscosity at different shear rates using the de-Guzman (Arrhenius) relationship. The flow curves and the viscosity–shear rate relationships were described by the Ostwald's and the Carreau's equations [11]. The maximum aging (contact) time of phases was 24 h. Characteristic Hungarian, but mostly the Battonya crude oils (Ba-55 and Ba-65) were applied as models in order to demonstrate the great variety of interfacial rheological properties. Origin and some physical and chemical properties of these oils are listed in Table 1. According to the earlier studies the Ba-55 oil/water system represents an average behavior in respect to both the absolute interfacial viscosity and its shear rate dependency [12]. Before contacting the oil phase with water in the sample holder, the oil was dewatered by centrifugation and in column filled with CaCl_2 . Ethoxylated nonyl-phenols with ethoxy group number between 10 and 40 were used as non-ionic surfactants. Micellization, structure of micelles and tenside solutions, and the thermodynamic parameters of micellization of the same surfactants under similar

experimental conditions were extensively studied earlier [13–16].

Results and discussion

At the boundary of two immiscible liquids, the free energy of a system diminishes considerably on formation of monomolecular films, rigid membranes, etc., if distinguished components of the oil phase are enriched in the boundary layer. Moreover, it is characteristic of rigid films that the number of molecules leaving the interfacial layer by diffusion is negligible as compared with those in the boundary layer [17]. It has already been shown for oil/water systems in the beginning of the 1950s that high molecular weight natural surfactants containing heteroatoms become highly enriched in the interfacial layer, and their presence considerably diminishes interfacial tension [18]. Owing to the composition of crude oils, the interfacial layer formed is generally of composite character, multicomponent and heterogeneous. In many cases a penetrated film containing also asphaltene particles is formed. On the other hand, the high viscosity of the hydrocarbon phases usually makes the diffusion a decisive factor in formation of an interface. Thus, depending on the concentration and nature of amphipathic compounds present in the crude oil, and on the viscosity of the bulk phases, different times are required for development of an interfacial layer and for attaining equilibrium state. Consequently, the interfacial rheological properties show simultaneously both time and temperature dependent features.

Although the problems of interfacial rheology was summarized in the excellent monograph by Joly [17, 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 properties during the flow of crude oils in porous media.

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

Character	: paraffinic
Formation depth, m	: 950–995
Age of reservoir	: lower Pliocene
Density*, g cm^{-3}	: 0.80
Viscosity**, mPa s	: 3.80
Atmospheric dist., %	: 33.00
Vacuum dist., %	: 57.00
Dist. residue, %	: 8.40
Asphaltene cont., %	: 1.90
Resin cont., %	: 0.20

*At 298 K.

**At 303 K.

Characterization of different crude oil/water systems

Fundamental interfacial rheological properties of different Hungarian crude oil/water systems were partly discussed earlier [12]. On the basis of the recent extensive studies the following general conclusions can be drawn:

- 1) The viscosity of interfacial layers may change within extremely wide limits (10^{-2} – 10^4 mN s m^{-1}) and this range is much greater than those found by interfacial tension measurements (Fig. 1).

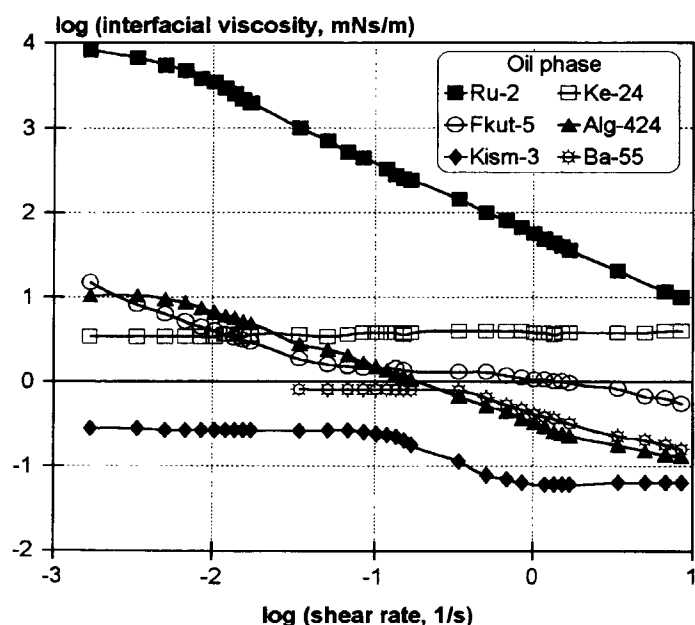


Fig. 1 Dependence of the interfacial viscosity on shear rate in case of different oil/water systems (dist. water; $t = 1$ h; $T = 303$ K)

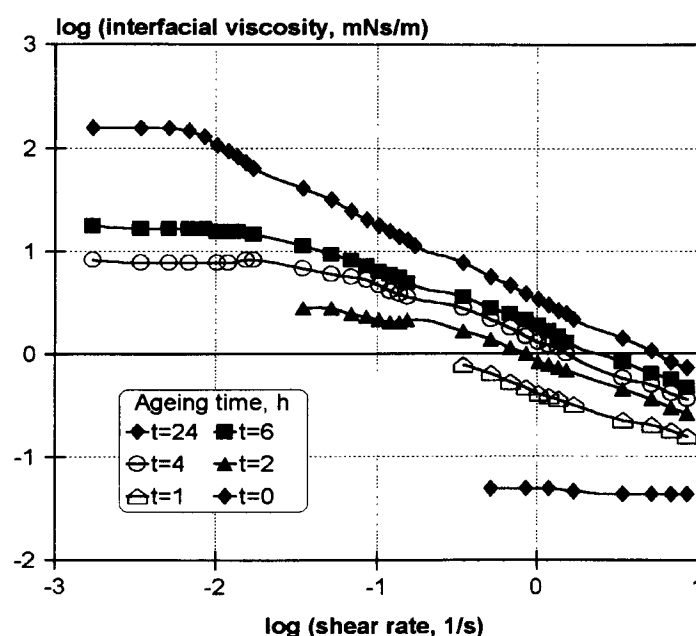


Fig. 2 Effect of aging time on interfacial viscosity (Ba-55 oil/dist. water system; $T = 303$ K)

- 2) The non-Newtonian flow behavior is general for all systems, however, sometimes a relatively long Newtonian section on flow curves is also characteristic. The shape, the location and the intersection point (rotation relaxation time) of Newtonian and non-Newtonian regions and the slope of the later one (shear thinning index) show great variability and individuality (Fig. 1).
- 3) The viscosity is usually increasing and the non-Newtonian flow behavior is strengthening with the aging time (Fig. 2). Similarly, the change of the shear thinning index and the rotation relaxation time reflects the gradual buildup of the internal structure and the enhanced chemical and mechanical interactions in the boundary layer (Table 2).
- 4) Time dependency of the interfacial rheological properties significantly depends on the type of crude oils: in certain cases the equilibrium sets within 1 h, but for medium and heavy oils more than 4 h is needed to reach constant values. Since these observations contradict the interpretations based on interfacial tension measurements (where max. 30 min is enough to set equilibrium), it seems necessary to reevaluate our theories on kinetics of formation of interfacial layers.
- 5) Although some chemicals influence simultaneously both the interfacial tension and viscosity, and the change is sometimes parallel, these factors are independent properties. That statement is proved by the fact that the interfacial tension always decreases with the

Table 2 Effect of aging time on Ostwald's constants and rotation relaxation time

Aging time, h	n	k	τ_r , s
0	2.48	1.04	0.80
1	2.47	1.76	3.16
2	2.41	2.24	6.31
4	2.25	2.60	25.12
6	2.13	2.83	56.23
24	1.70	3.63	177.82

aging time, while the viscosity changes in the opposite direction.

- 6) 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, meanwhile the basic non-Newtonian flow behavior usually remains unchanged.
- 7) The interfacial viscosity decreases with temperature. The dynamics of change is influenced, however, by the shear rate and the aging time. The greatest change, relatively speaking, is observed in the low shear rate range and close to the interfacial equilibrium. At the same time the non-Newtonian character of the flow curves is gradually depressed at elevated temperatures.
- 8) Activation energy of the viscous flow decreases with increasing shear rate and decreasing aging time (Fig. 3). This fact implies that a relatively thick layer of stable

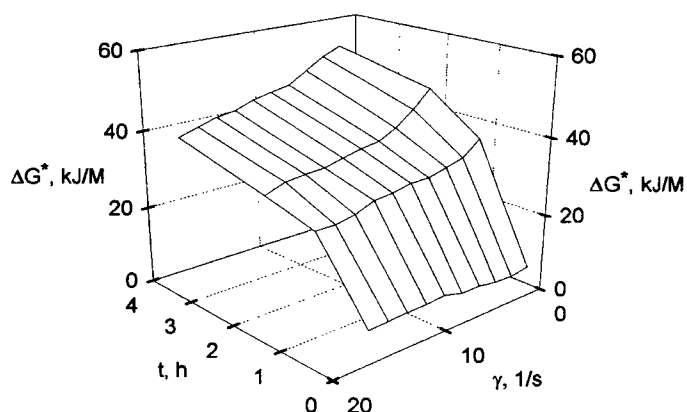


Fig. 3 Dependence of the activation energy of the viscous flow on aging time and shear rate (Ba-55 oil/dist. water system; $T = 303\text{ K}$)

structure forms at rest, which can be disintegrated only by high shear force. In the dynamic state, or in a period of incomplete structural buildup however, much less deformation force is needed to break up the chemical and mechanical interactions in the layers, or to modify the structure of oil/water interfaces.

The interfacial rheological studies have definitely shown that all properties (viscosity, non-Newtonian flow behavior, shear thinning index, rotation relaxation time, activation energy of viscous flow and their shear rate, aging time and temperature dependency) are individual factors which might be used for identification and characterization of different oil/water systems (reservoirs and even wells). Further, the interfacial rheological properties are equally important parameters of the interfaces as the interfacial tension and the wettability are. It was also clearly proved that the enhanced oil recovery methods (and colloid technologies in a wider sense) cannot be investigated and developed without precise analysis of the effect of chemicals to be applied on these parameters.

Effect of surfactants on interfacial rheological properties

The surfactant or micellar flooding is based on the drastic (4–5 orders of magnitude) interfacial tension lowering effect of tensides. Mobilization of oil is a consequence of partial or total solubilization of entrapped or residual oil in pore spaces and formation of mobile microemulsions in the reservoirs. Preferential adsorption of tensides at the interface is in the background of the phenomena, viz. the active monomers (rarely micelles) of surfactant are able to displace the originally adsorbing molecules present in crude oils from the boundary layers. Since the process is followed by a measurable decrease or weakening of the

intermolecular interactions and the structural modification of the layers, it can be predicted that the interfacial rheological properties will also change significantly. To prove this expectation the effect of ethoxylated nonyl-phenol homologues used widely in oil field chemistry were studied in a specific crude oil/water system (Ba-55 oil). The preliminary observations were briefly reported earlier [20].

Effect of tenside concentration

In the first test series the effect of tenside concentration was determined. The measurements were carried out in a concentration range of $0\text{--}1\text{ g l}^{-1}$. The critical micellization concentration of these compounds are highly dependent on the ethoxy group number and the temperature [13]. Taking values in Table 3 into account, the tested concentrations were below and above the c.m.c. To demonstrate the effect of tenside concentration on interfacial viscosity the limiting cases (NPEO₁₀ and NPEO₄₀) are shown in Fig. 4 and the observations can be summarized as follows:

- 1) The non-ionic surfactants have a drastic impact on interfacial viscosity and the change exceeds some orders of magnitude.
- 2) The non-Newtonian flow behavior gradually diminishes with tenside concentration. At high tenside concentrations, particularly in case of slightly ethoxylated non-ionic surfactants, the viscosity-shear rate relationship shows dilatant characteristics, while in the presence of highly ethoxylated nonyl-phenols at the same concentrations, the plastic behavior remains the ruling tendency.
- 3) The measurements, using continuous shearing at constant shear rates, also revealed that the dilatancy is strengthening over in time, viz. the dilatant flow behavior can probably be traced back to forced emulsification in the interfacial layer itself and in the nearby bulk region.

Table 3 Critical micellization concentration of the analyzed tensides

Tenside	c.m.c.	
	$10^{-5}\text{ mol l}^{-1}$	g l^{-1}
NPEO ₁₀	7.48	0.05
NPEO ₂₀	12.30	0.14
NPEO ₃₀	15.07	0.23
NPEO ₄₀	20.30	0.40

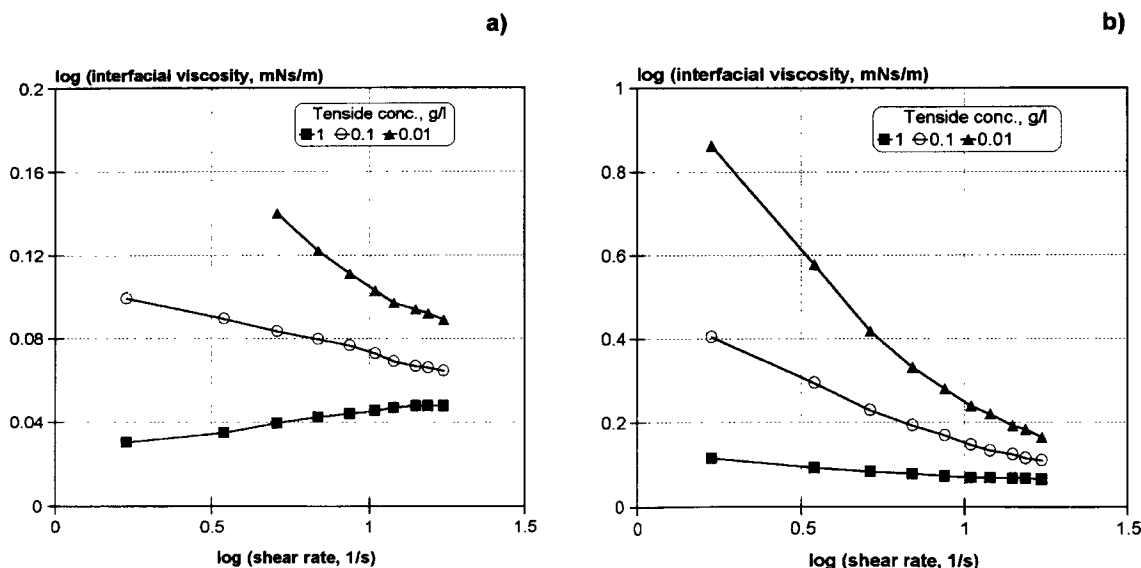


Fig. 4 Effect of tenside concentration on interfacial viscosity (Ba-55 oil; a) NPEO₁₀; b) NPEO₄₀)

Thus, the rheological behavior of interfacial films can be categorized by the critical micellization concentration. Below the c.m.c. a drastic decrease in interfacial viscosity and depression of non-Newtonian flow behavior is characteristic and these changes reach limiting values in vicinity of c.m.c. Above the c.m.c. the interfacial viscosities are in range of 0.01–0.1 mNs m⁻¹, and the effect of concentration is negligible and the interfacial layers are almost Newtonian. The results also indicated a pronounced dilatancy with decreasing ethoxy group number which can probably be explained by the fact that the relatively weak hydrophobic interaction becomes the ruling force in shaping the structure of the boundary layers.

Effect of ethoxy group number

Mass and size of micelles significantly depend on the ethoxy group number of non-ionic tensides [14]. Since the oriented adsorption of monomer molecules in the interfacial layer is also closely connected with the length and the hydration state of the hydrophilic side chain, the packing density is also influenced by steric effects. Accordingly, the ethoxy group number might be considered as a key factor in shaping of the interfacial rheological properties of the oil/water systems.

The detailed studies performed at different shear rates and aging times made it possible to draw the following conclusions:

- 1) Using identical tenside concentrations the tensides with a high ethoxy group number have a much smaller effect

on interfacial viscosity than the slightly ethoxylated nonyl-phenols. The positive effect decreases monotonically with the ethoxylation. Similarly, the non-Newtonian flow behavior remains predominant in case of NPEO₃₀ and NPEO₄₀, while it is practically absent when NPEO₁₀ is present in the aqueous phase. The characteristic effect of ethoxy group number appears definitely at a short aging time, even at $t = 0$ h as shown in Fig. 5.

- 2) The crucial effect of ethoxy group number becomes stronger at long aging times, but surprisingly the “aging phenomena” (increase in viscosity, or strengthening of its shear dependency) could not be observed for NPEO₁₀.
- 3) In the presence of highly ethoxylated homologues the dynamics of aging seems to be significant, through modification of the interfacial rheological properties is less pronounced than in tenside-free systems. This fact implies that setting an interfacial equilibrium in tenside-containing systems needs shorter time than in distilled water, however the structure of the layer formed is also less complex, thinner and well structured.
- 4) The characteristic effect of the ethoxy group number decrease rapidly with temperature. The shape of the response surfaces shown in Fig. 6 clearly prove that parallel with the decreasing viscosity, and weakening non-Newtonian flow behavior, the dependence of these parameters on ethoxy chain length ceases gradually. Practical consequence of these phenomena is that under reservoir conditions (e.g. > 363 K) the interfacial rheological properties, and hence the emulsification of

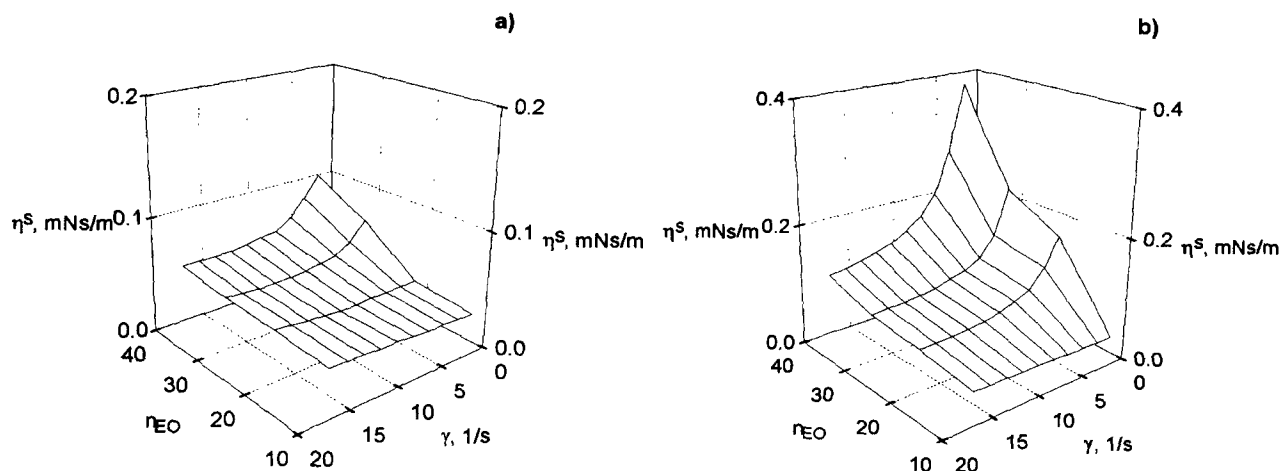


Fig. 5 Dependence of the interfacial viscosity on ethoxy group number and shear rate (Ba-55 oil; $c_s = 1 \text{ g l}^{-1}$; $T = 303 \text{ K}$; a) $t = 0 \text{ h}$; b) $t = 4 \text{ h}$)

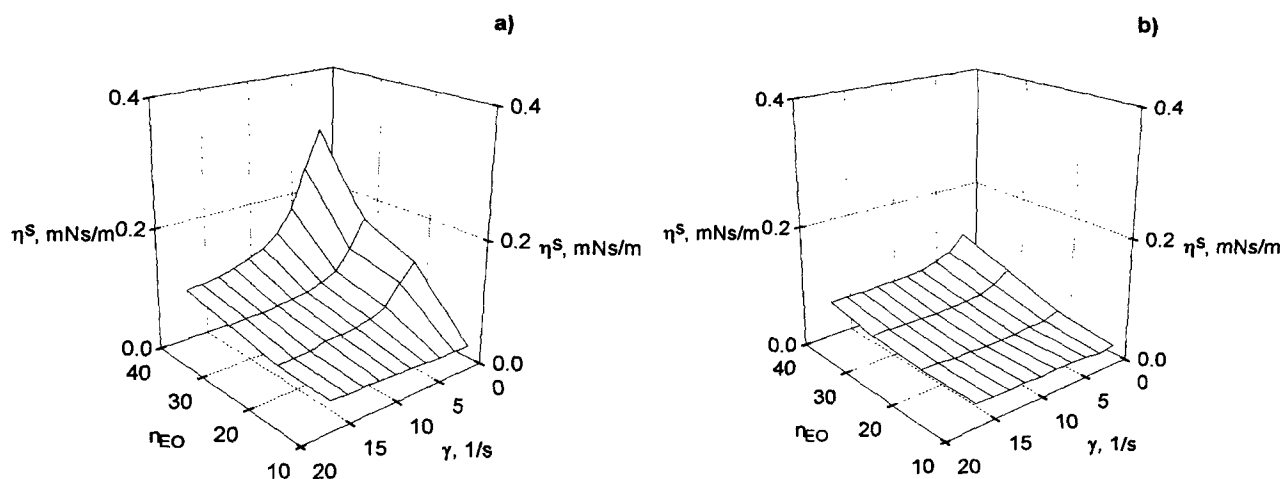


Fig. 6 Dependence of the interfacial viscosity on ethoxy group number and shear rate (Ba-55 oil; $c_s = 1 \text{ g l}^{-1}$; $t = 4 \text{ h}$; a) $T = 313 \text{ K}$; b) $T = 323 \text{ K}$)

phases and stability of the dispersed systems, will become invariant to the type of the tensides if they differ only in the ethoxy chain length.

The experimental results can closely be related with the earlier findings [13–16]. Namely, the surfactant homologues having the same hydrophobic nucleus, but shorter ethylene oxide chain, form micelles of higher molecular weight (aggregation number) and size and by the change of the second virial coefficient it may be presumed that the stability of such tensides (partly because the monomer solubility in aqueous media is poorer) is also greater than in cases of tensides having longer hydrophilic side chains. In this way a logical explanation of the observations is that

the concentration and the packing density under the given conditions is maximal in the presence of NPEO₁₀ and minimal when NPEO₄₀ is dissolved in the aqueous phase. However, the difference between these limiting cases is diminished at elevated temperatures.

The faster set of interfacial equilibrium in the presence of non-ionic surfactant, particularly at elevated temperature, may allow us to conclude that the earlier interpretation of the effect of tensides on interfacial rheological properties must be reconsidered. According to the widely accepted idea, the surfactant molecules are able to “displace” the preliminary adsorbed natural amphipatic molecules from the interface. In the mirror of the present results it seems more plausible that first the smaller and

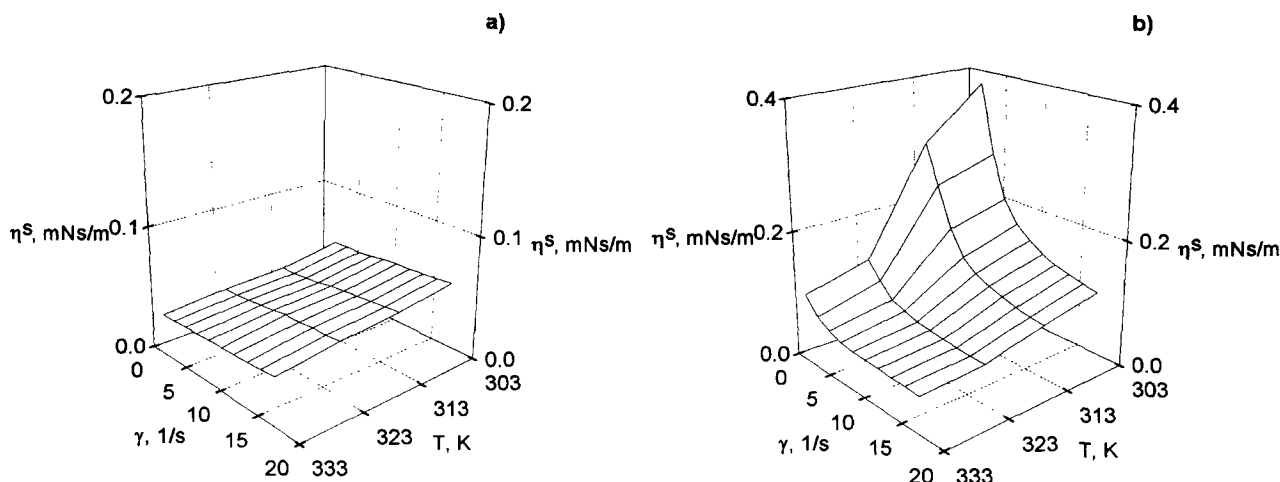


Fig. 7 Dependence of the interfacial viscosity on shear rate and temperature (Ba-55 oil; $c_s = 1 \text{ g l}^{-1}$; a) NPEO₁₀; b) NPEO₄₀)

more mobile surfactant molecules form a dense monolayer, and thus, formation of a hydrophobic environment towards the hydrocarbon phase prevents the accumulation of those high molecular weight, natural surface active agents in the interface which are always present in crude oils and responsible for the rigid film formation.

Effect of temperature

The effect of temperature on interfacial rheological properties was partially discussed in the previous section. That picture is completed by Fig. 7 where the interfacial viscosity is plotted against the shear rate and the temperature for NPEO₁₀ and NPEO₄₀, respectively. Both response surfaces belong to $t = 4 \text{ h}$ aging time. Comparing the curves here it is convincingly proved that extremely low interfacial viscosity and practically non-Newtonian flow behavior can be attained in oil/water systems by proper selection of the tenside to be applied, meanwhile the shear rate and temperature dependency of interfacial properties can also be depressed to a negligible level.

The fundamental effect of temperature could be expected on the basis of the thermodynamic data of micellization in the same tenside solutions [13, 15, 16]. The calculated H_m and S_m values are positive in the temperature range of 293–323 K, and that confirms the endothermic character of both the dehydration of the ethylene oxide groups and the destruction of the “iceberg” water structure developed in the environment of the hydrophobic part of the monomers when the aggregation (micelle formation) starts in the system. On the other hand, it was also found that the Gibb’s energy of micellization for

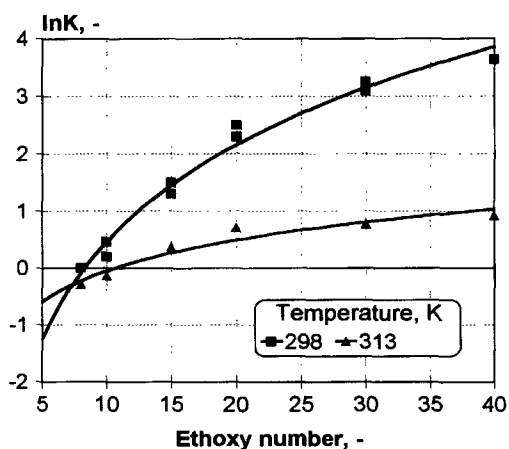


Fig. 8 Partition coefficient of ethoxylated nonyl-phenols in oil/water system at different temperatures (Ba-55 oil)

a given tenside is negative and its value is decreasing nearly linearly with temperature. Since G_m is smallest for NPEO₁₀, we may conclude that the strongest hydrophobic interaction, highest packing density and concentration in the interfacial layer ensues when this tenside is present in the oil/water system, particularly at elevated temperatures. This explanation is supported by the fact that the tensides with short ethoxy chain ($n_{EO} = 8$) are predominantly oil soluble, while the highly ethoxylated products ($n_{EO} = 20$) are expressively water soluble. This fact is indirectly proved by the partition coefficients determined for the same surfactants and oil/water system. As shown in Fig. 8 the partition coefficient is decreasing with the ethoxy group number and the curve intersects the $\ln K = 0$ axis

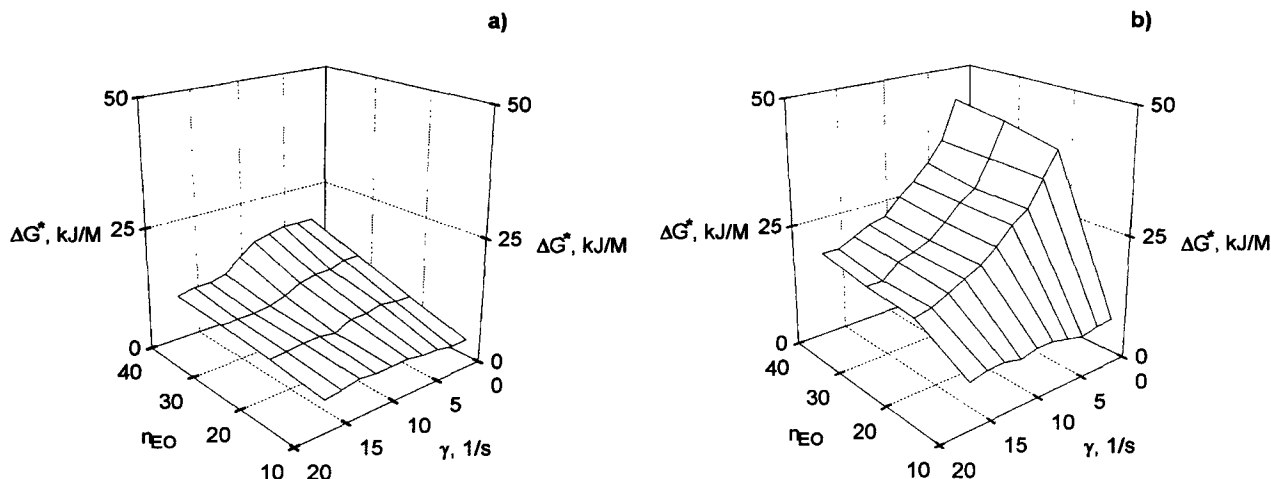


Fig. 9 Dependence of the activation energy of the viscous flow on ethoxy group number and shear rate (BA-55 oil; $c_s = 1 \text{ g l}^{-1}$; **a)** $t = 0 \text{ h}$; **b)** $t = 4 \text{ h}$)

between $n_{EO} = 8$ and 10. The solubility of tensides further increases at elevated temperatures on account of dehydration of the ethoxy chain. Namely, latter tensides are already partially soluble in both the aqueous and the oil phases implying that the interfacial tenside concentration becomes maximal under that circumstances.

Activation energy of the viscous flow in the presence of tensides

Calculation of the activation energy of viscous flow (Gibb's energy of the viscous flow according to the Eyring's theory) provided additional arguments to the previous interpretation and confirmed the statements made until now. Dependence of G^* on ethoxy group number and shear rate can be seen in Fig. 9. In good agreement with the behavior of other interfacial rheological properties the variation of this thermodynamic parameter may allow the following conclusions;

- 1) At short aging time ($t = 0 \text{ h}$) the activation energy scarcely depends on the type of tensides and the shear rate. However, the value of G^* apparently decreases with the shear rate.
- 2) In a medium state of structural buildup of the interfacial layer the activation energy of tensides, except the NPEO₁₀, increases by 20–40%. In the equilibrium state of the interfacial layer, the energy consumption of irreversible deformation becomes already two or three times greater than at $t = 0 \text{ h}$ aging time. The NPEO₁₀ represents an exception again in all respects: neither a measurable increase in activation energy, nor

strengthening of its shear rate dependency could be detected as a function of aging time.

- 3) It is surprising that the activation energy significantly increases and its shear dependence gets drastically stronger with aging time though, the ethoxy group number has only a negligible impact on G^* at any experimental conditions, even at long aging times.

The phenomena can be explained by the structural difference of layers. The shear rate dependent feature of activation energy, particularly in the case of highly ethoxylated homologues, suggests that part of the activation energy is consumed by the elastic deformation of the structure and the disintegration of the intermolecular interactions existing in the interfacial layer at rest. Reasonably, the absolute values and the change of the actual activation energies may serve as a reliable basis for prediction of the emulsion stability or, the propensity and rate of coalescence. For instance, the activation energy might be accepted not only as a qualitative, but a quantitative parameter of the mentioned processes. Obviously, the high activation energy of the viscous flow render the stable emulsions hard to break, while activation energies less than 5 kJ mol^{-1} imply that the two-phase systems readily emulsify, but they easily or spontaneously break at rest.

Conclusions

Interfacial rheological studies of oil/water systems in the presence of ethoxylated nonyl-phenols made allow to

conclude the following:

- 1) The interfacial viscosity of different oil/water systems may differ by 5–6 orders of magnitude, the interfacial films are highly non-Newtonian and all rheological properties depend significantly on aging time and temperature.
- 2) In the presence of non-ionic surfactants the interfacial viscosity and the activation energy of the viscous flow decrease considerably and the interfacial layers become nearly Newtonian, meanwhile the dependency of the interfacial properties on aging time and temperature also diminishes. The positive effect of the surfactants increases with decreasing ethoxy group number of the tenside.

The results could be explained satisfactorily through micellization phenomena of the same tensides in aqueous phase and their preadsorption in the interface. As a summary it was evidenced that the interfacial rheology is an efficient and powerful detection technique, which may enhance our knowledge on formation, structure, properties and behavior of interfacial layers formed in oil/water systems. Therefore, interpretation of the interfacial

rheological properties will probably contribute to the extension of the weaponry of the reservoir characterization, better understanding of the displacement mechanism, development of more profitable EOR/IOR methods, intensification of the surface technologies. Similar studies will, however, accelerate also the progress in all areas of colloid science and technology.

Glossary of symbols

c_s	tenside concentration, g l^{-1}
k	preexponent constant, – (Ostwald's constant)
n	shear thinning index, – (Ostwald's constant)
n_{EO}	ethoxy group number
t	aging time, h
ΔG^*	activation energy of the viscous flow, kJ mol^{-1}
K	partition coefficient
T	temperature, K
γ	shear rate, s^{-1}
η_s	interfacial viscosity, mN s m^{-1}
τ_r	rotation relaxation time, s (Carreau's constant)

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