INVESTIGATION OF CRUDE OIL-WATER EMULSIONS. IN PRESENCE OF NON-IONIC SURFACTANTS, I.

Behaviour of emulsions at room temperature and in ion-free systems

By

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The investigations were aimed at determination of the emulsion-forming ability of surface-active agents suitable for oil displacement, and within this, the effects of the type and relative quantity of the tensides and of the phase ratio on the properties of the emulsions. Crude oil was used, with 4-ethoxy-nonylphenolsulphonate as the anionic tenside, and nonylphenols with different ethoxy group numbers as the non-ionic ones.

From the experimental results it was concluded that stable and high-viscosity oil-external emulsions were formed in the system free of tensides. With increasing concentration of surfactants having low HLB values, the plastic viscosity of the emulsions decreased, while at a characteristic concentration phase inversion took place. With tensides having high HLB values, similar changes in rheological properties occurred, but phase inversion was not observed. This anomalous behaviour of the emulsions is attributed to the interaction of the synthetic and natural surface-active agents present in the crude oil.

Introduction

During the application of conventional and enhanced oil recovery methods, the formation of emulsions often takes place [1]. Emulsions are usually formed under the mechanical effect of flow, by the oil entering the well and by the layer body. The dispersion effect is enhanced by the gas likewise entering the well and by the flow through the jets regulating the well's output. However, the stability and rheological characteristics of the resulting emulsions are determined not by the circumstances of primary emulsification, but rather by the chemical composition of the oil produced [2]. Water, gas, polymer or tenside solutions injected into the layer during the secondary and tertiary oil recovery also contribute to the probability of emulsification. The emulsions thus formed can influence the efficiency of oil recovery considerably. From this point of view, the nature, drop size, drop-size distribution, stability and rheological characteristics of emulsions are of decisive importance [3].

If the emulsified drops are small in size and the emulsion has high drop and distribution constancies, the recovery will not be influenced essentially, but the separation of the oil from the water will be difficult [4]. On the other hand, if the drop

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size is comparable with that of the pores, the drops will move along at a rate considerably lower than that of the displacing fluid, thereby hampering the control of mobility. Emulsified drops may even be resident in narrow pores, resulting in such cases in a plug effect and a reduction to zero flow rate along this section [5].

General scope of investigation — application of surfactants in enhanced oil recovery

The surfactants applied during tertiary recovery can be stabilizers of emulsion formation. However, the utilization of surfactants to increase oil recovery is not a novel technique. As early as in 1929, DE GROOT [6] applied for a patent on the use of a water-surfactant system to increase oil recovery, and HOLBROOK [7] had surface-active substances of various chemical compositions, both non-ionic and ionic ones, patented for the same purpose.

In selecting the surfactant to be used, one has to take into account its emulsifying effect on water, the nature of the emulsion formed, and its stability and rheological properties. In the literature a great number of data have been published on the effects of surfactants as emulsifiers on emulsion properties, but the investigations were carried out mainly with model substances. BANCROFT [8], in 1913, found that the nature of the emulsion is determined in a decisive manner by the emulsifying agent, and that the phase in which the emulsifier is more readily dissolved will be the dispersion medium.

A practical aid for selecting the most suitable emulsifying agent is provided by the HLB scale, proposed for non-ionic surfactants by GRIFFIN [9] and further developed by DAVIES [10].

The HLB value of non-ionic surfactants may be influenced by several factors. According to SHINODA [11], the HLB value depends on the nature of the oil phase and on the additional agents dissolved in the water and the oil, a further important role being played by temperature, as this basically affects the interaction between the hydrophilic portion of the emulsifier and the water, as well as that between its lipophilic portion and the oil. MARSZALL [12] proposes that the HLB value varies with temperature, entailing as a result a change in the cloud-point of the tenside as well, which is manifested at different temperatures as a function of the solvent and the dissolved materials. Consequently, the emulsions stabilized with non-ionic emulsifiers are of o/w (oil in water) type at lower temperatures, and of w/o (water in oil) type at higher temperatures. The temperature at which inversion occurs is the phase inversion temperature (PIT), where the hydrophilic and lipophilic properties of the tenside are just in equilibrium [13].

As pointed out by SHERMAN et al. [14], the nature of an emulsion depends not only on the quality of the emulsifier, but on its relative amount as well. With emulsions having a high oil content, a low emulsifier concentration gives rise to an emulsion of w/o type, while emulsions of o/w type are formed at relatively high emulsifier concentrations. At the same time, a type of non-ionic tenside exists which lends itself to the preparation of variants having quite different HLB values, but the emulsions stabilized by them are always of o/w type. Such an application of the HLB system becomes questionable when mixtures of emulsifying agents are used to evaluate the nature of emulsions.

The rheological properties of emulsions depend on the viscosities of the disper-

sion medium and the dispersed portion, the volumetric concentration of the latter, the quality and quantity of the emulsifying agent, and the degree of dispersity [15]. Emulsions also differ greatly in their rheological properties, depending on which of the phases making up the emulsion represent the dispersion medium and the dispersed portion, respectively. Attempts have been made to describe the relationship between the viscosity of the emulsion and the volumetric fraction of the dispersed portion by various power functions, but none of the published relationships may be regarded as having absolute validity [15, 16, 17].

RICHARDSON [18] and JOHN [19] have considered the relationships between the drop size and drop-size distribution and the rheological characteristics.

The effects of the quality and quantity of emulsifiers on the viscosity and the phase inversion temperatures of emulsions were studied in detail by SHERMAN [16]. *Inter alia* it was concluded that the relative quantity of tenside influences the rheological properties of emulsions to a considerable extent if the volumetric ratio of the emulsion is over 0.5. However, the phase inversion temperature always changes with the tenside concentration, and in the vicinity of PIT the viscosity exhibits a maximum.

In the literature, mainly the properties of emulsions prepared from model materials are dealt with. These research data cannot be adapted unconditionally to emulsions prepared directly from crude oil and water or aqueous solutions of tensides. For this reason, we set out to investigate in detail the factors influencing the properties of emulsions prepared by using crude oil. In this paper the relationships between the phase ratio, the quantity and quality of surface-active materials dissolved in the aqueous phase of the emulsions and the nature and the rheological properties of the emulsions are discussed.

Experimental

Materials

A crude oil from the Algyő-2 well was used as the oil phase of the emulsions, and distilled water and aqueous tenside solution, respectively, served as the aqueous phase. The tensides applied were nonylphenol — ethylene oxide adducts (NPE_x) of non-ionic character, made by the Dow Chemical Dompany, in which the number of ethylene oxide groups varied between 8 and 40. The anionic tenside (A) was a derivative of 4-ethoxynonylphenol, in sulphonated form, made by Servo Chemische Fabriek. The HLB values for the tensides were calculated by the DAVIES formula [10] and their critical micellar concentrations were determined from the surface tensions of solutions, measured with a Du Noüy tensiometer. These data are listed in Table I.

Methods

The emulsions were always prepared by the same method. The tenside was dissolved in the aqueous phase and dispersed. Upon mixing of the oil and aqueous phases, the

Table I

HLB and c.m.c. values of emulsifiers

Symbol of emulsifier	HLB	c.m.c. 10^{-4} mol
NPE_8	3.8	0.78
NPE_{10}	4.5	0.67
NPE_{15}	6.1	1.00
NPE_{20}	7.8	1.66
NPE_{30}	11.1	2.29
NPE_{40}	14.4	2.24
A	—	1.63

system was stirred for 10 minutes under thermostating at 298 K, using a UNIPAN type 309 homogenizer operating at 2800 rpm.

The nature of an emulsion was determined by the dilution test, but this could also be decided upon on the basis of the colour of the emulsion.

A RHEOTEST-2 rheoviscometer and an S1 measuring system were used in the rheological studies. The shear rate (D) was varied in 12 steps within a range of 1.5 and 656 s^{-1}. The shear stress (τ) varied between 0 and 230 Pa. The legs of flow curves obtained with both increasing and decreasing shear rate values were determined. The Bingham yield value (τ_B) was obtained from the intercept of the final linear section of the flow curve. The plastic viscosity (η_{pl}) was calculated from the slope of the straight line, *via* the following relationship:

$$\eta_{pl} = \frac{\tau_{max} - \tau_B}{D_{max}}$$

where D_{max} = max. shear rate
         τ_{max} = shear stress measured at D_{max}
         τ_B = Bingham yield value.

Results and discussion

In the first stage of the research program emulsions with different phase ratios were prepared, using Algyő-2 oil and distilled water. The kinetic stability of samples prepared without emulsifier proved surprisingly high, with no dispersion medium or dispersed part separating from the system even at room temperature and after a standing time of one week. For each water-oil ratio (WOR), the stable emulsions were oil-external ones. If the quantity of water as dispersed portion exceeded 80 per cent, then the stability of the emulsion was reduced considerably. No stable water-external emulsion could be prepared without tenside.

Figure 1 shows the equilibrium flow curves for oil-external emulsions with different phase ratios, obtained with increasing shear rate.

It is obvious from Fig. 1 that, from a rheological point of view, the emulsions with a low water content are pseudoplastic systems, while those having a high water content are plastic ones having a definite yield value.

The plastic viscosity of the emulsions increases rapidly with the relative amount of water dispersed in the oil phase. This is illustrated by the experimental data relating to the w/o emulsions in Fig. 2.

In addition to this, Fig. 2 gives a comparison of the changes in the plastic viscosities of the w/o and o/w emulsions with the phase ratio. The o/w emulsions were prepared by using a non-ionic tenside, NPE$_{30}$. It may be stated on the basis of Fig. 2 that with the increase of the water content of the emulsion the plastic viscosity increases sharply in the case of the w/o emulsions, and decreases rapidly in the case of the o/w emulsions. Essentially the same can be concluded in connection with the Bingham yield values of the systems. The nature of the emulsions, *i.e.* whether the dispersion medium consists of oil or water, is of basic importance from the aspect of oil displacement.

The complete flow curves for tenside-free water-crude emulsions prepared with different phase ratios are demonstrated in Fig. 3.
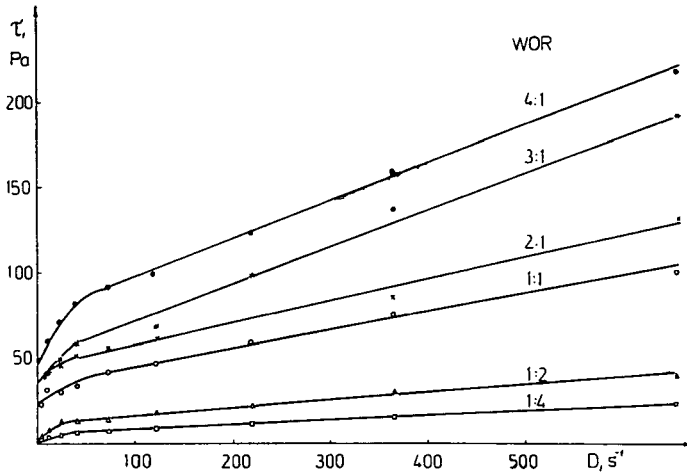
Fig. 1. Flow curves of oil-external emulsions prepared from Algyő-2 crude and distilled water at different water-oil ratios

It is seen from Fig. 3 that the flow curves obtained with increasing and with decreasing shear rates do not agree. The curve measured with increasing shear rate always lies above the curve obtained with a decreasing shear rate. If the system is investigated using the same shear rate, then shearing results in a structure degradation, and hence a reduction of shear stress takes place. In our experience, after an appropriate period of repose the initial shear stress values are regained by the system, and thus the coherent structure is rebuilt. This, however, points unequivocally to the phenomenon of thixotropy. If the hysteresis loop area is accepted as a measure of the thixotropy, then it may be stated that the extent of thixotropy (parallel with the plastic viscosity and the Bingham yield value) gradually increases with the increasing volumetric fraction of the dispersed portion.

Further, it was studied how the nature and rheological properties of the emulsions prepared from Algyő-2 oil are affected by the quantity and quality of the emulsifiers dissolved in the water. During the experiments the phase ratio was always 1:1. Each of the emulsifiers listed in Table I, even when used in small quantities, reduces the viscosity and structural strength of the emulsions to a considerable degree; however, up to a characteristic tenside concentration, the emulsions always have a w/o character. No serious deviation of the flow curves may be observed from those given in Fig. 1, but the plastic character reduces as the quantity of tenside increases, and the majority of the systems become pseudoplastic ones. Formation
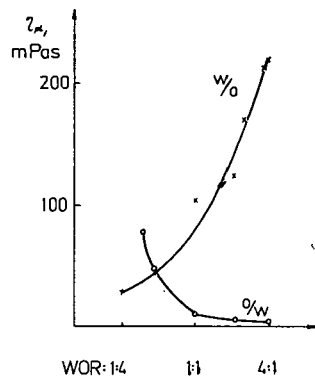

Fig. 2. Plastic viscosities of an oil-external emulsion made from Algyő-2 crude oil and distilled water, and a water-external emulsion prepared from crude oil and 3.5% NPE_{30} plotted as a function of the water-oil ratio
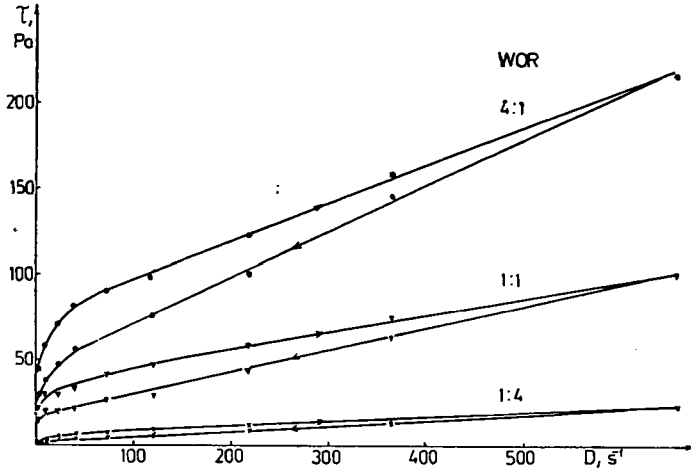
Fig. 3. Flow curves of Algyő-2 oil distilled water emulsions
at different water-oil ratios

of stable oil-external emulsions is therefore an unfavourable phenomenon as far as the oil recovery is concerned.

The use of non-ionic tensides having relatively few ethylene oxide units with small HLB values and anionic tensides in a certain well determined quantity always gives reproducible emulsions of o/w type.

As concerns the rheological properties, the o/w emulsions prepared with a phase ratio of 1:1 show only low pseudoplasticity, with a minimum plastic viscosity, which changes only slightly with the increase in the quantity of emulsifier. This is illustrated by the experimental data in Figs. 4—8, where the plastic viscosity of the emulsion is plotted as a function of the emulsifier concentration.
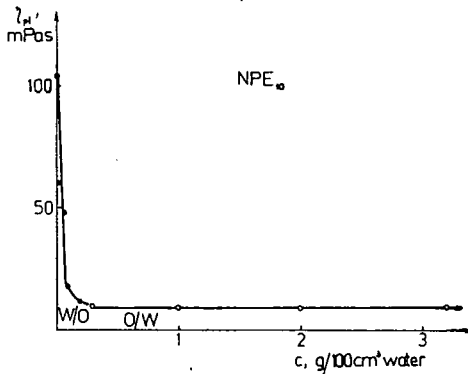

Fig. 4. Plastic viscosity of emulsions stabilized by NPE_{10} vs. tenside concentration (WOR = 1:1)

In Fig. 4, the plastic viscosity of an emulsion prepared with NPE_{10} is plotted as a function of the emulsifier concentration. It can be stated that up to an emulsifier content of 0.2% the emulsion always has a w/o character. If the emulsion is prepared using an emulsifier quantity greater than this, an emulsion of o/w type results. The amount of tenside required to produce an o/w emulsion gradually increases with increasing ethylene oxide content and HLB value of the tenside. Of the non-ionic tenside NPE_{15} (Fig. 5), 0.7% is needed (at a phase ratio of 1:1) to bring about an o/w emulsion using Algyő-2 oil, while of the emulsifier containing 20 ethylene oxide units (Fig. 6), as much

as 2.6% is needed. If a tenside containing 30 or 40 ethylene oxide units is used (Fig. 7), then, in the concentration range investigated, we always obtain a *w/o* emulsion.

These experimental results seem to contradict the generally known and published findings relating to emulsions and non-ionic emulsifiers, respectively [15—16], according to which emulsions of *w/o* type are stabilized primarily by emulsifiers with small HLB values, and those of *o/w* type are stabilized by emulsifiers having large HLB values. However, there are also references in the literature [14, 17—18] that call attention to the contradiction between the HLB value and the emulsifying ability, namely that the emulsion type may also vary with the relative amount of emulsifier. These statements, of course, relate only to emulsions produced from pure, single-component phases. In our instance, however, the Algyő-2 crude is a mixture of
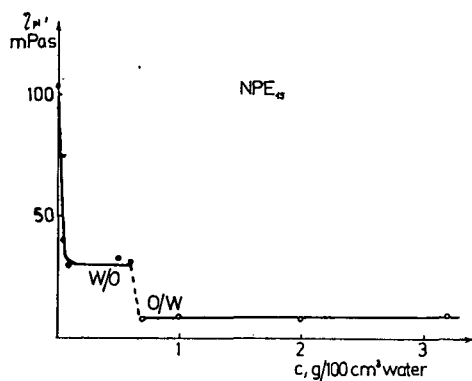
Fig. 5. Plastic viscosity of emulsions stabilized by NPE_{15} *vs.* tenside concentration (WOR = 1:1)
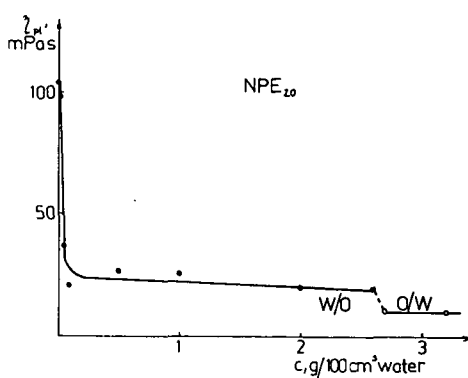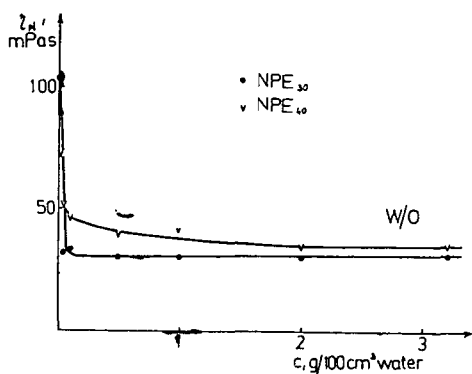
Fig. 6. Plastic viscosity of emulsions stabilized by NPE_{20} *vs.* tenside concentration (WOR = 1:1)

Fig. 7. Plastic viscosity of emulsions stabilized by NPE_{30} or NPE_{40} *vs.* tenside concentration (WOR = 1:1)
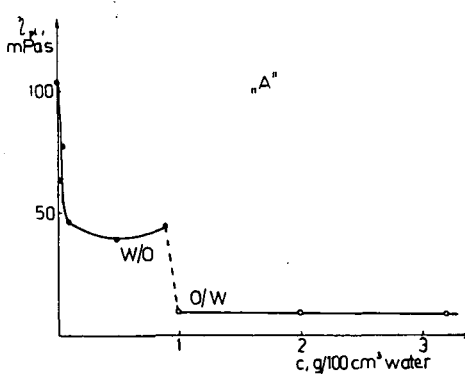
Fig. 8. Plastic viscosity of emulsions stabilized by anionic emulsifier (A) *vs.* tenside concentration (WOR = 1:1)

hydrocarbons of different compositions and structures. The interaction between the tenside and crude components, not easily amenable to quantitative treatment, may account for the fact that emulsions of w/o and o/w type alike can be prepared with a given tenside, depending on its relative quantity. Likewise attributable to this is the fact that a stable o/w emulsion is formed by a tenside with a low ethylene oxide number and a small HLB value (Table I), which stabilizes mainly w/o emulsions if pure components are used. As concerns the tensides with large HLB values generally known as o/w emulsifiers, they stabilize only w/o emulsions if Algyő-2 oil is used (Fig. 7).

The anionic tenside investigated exerts an emulsifying effect similar to that of the non-ionic ones having small HLB values (Fig. 8). When used in small quantities, it reduces the plastic viscosity of the oil-external emulsions; in a considerable concentration range, no change in viscosity occurs, yet the emulsions are sill unmistakably of w/o type. From a well-defined emulsifier quantity (0.9%) onward, the emulsions having a phase ratio 1:1 and prepared with Algyő-2 oil are always water-external ones.

In the series of tests illustrated in Figs. 4—8, the effects of the quality and quantity of the emulsifier on the type of the emulsion were investigated; in the experiments the phase ratio of 1:1 was left unchanged. It seemed advisable to investigate the effects of the phase ratio on the type and plastic viscosity of the emulsions for the same emulsifier quantity. In the series of tests shown in Fig. 9, the emulsifier concentration was 0.1%.

On the basis of the results summarized in Fig. 9, it may be stated that, when a tenside having a small ethylene oxide number and a small HLB value (NPE$_{10}$) is used, the change in the emulsion type takes place at a larger oil content than in the case of a tenside of large HLB value (NPE$_{30}$). The anionic tenside investigated occupies an intermediate position between the two non-ionic emulsifiers. It is also obvious from the Figure that the plastic viscosities of oil-external emulsions prepared by using tensides having the same phase ratio but a different ethylene oxide number show great differences. The difference is especially great in the case of phase ratios near the phase reversal. The plastic viscosity of an emulsion prepared with NPE$_{30}$ tenside is about
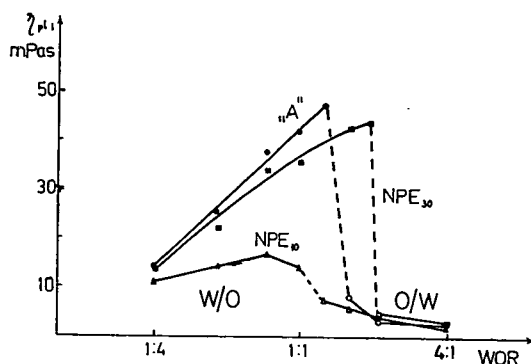

Fig. 9. Plastic viscosity of emulsions stabilized by different emulsifiers plotted as a function of phase ratio (Concentration of emulsifier: 0.1 g/100 cm³ emulsion)

three times as much as it would be if the same quantity of NPE_{10} emulsifier was used. At the same time, the plastic viscosities of the water-external emulsions agree with one another to a good approximation.

If, in the case of a given emulsifier quality, the effects of its quantity on the plastic viscosity and the type of the emulsion are investigated (Fig. 10), it may be stated that the plastic viscosity of an emulsion decreases as the emulsifier concentration increases. If larger quantities of emulsifier are used, the phase inversion will take place at lower water contents, and hence water-external emulsions will result.
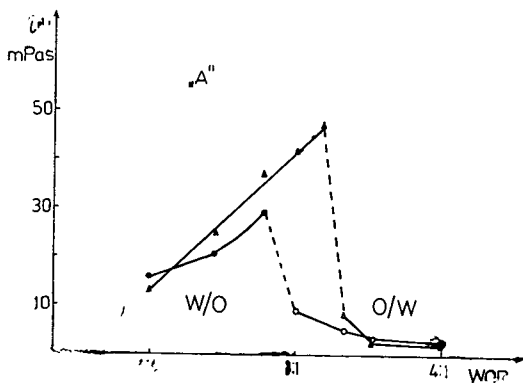

Fig. 10. Plastic viscosity of emulsions stabilized by anionic surfactant at different concentrations
▲ 0.1 g/100 cm³ emulsion, ● 1.0 g/100 cm³ emulsion

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ИЗУЧЕНИЕ ЭМУЛЬСИЙ СЫРОЙ НЕФТЫ В ПРИСУТСТВИИ НЕИОННЫХ ДЕТЕРГЕНТОВ, I.

Б. Фелиан, Я. Балаж, И. Лакатош

Исследование предпринято с целью установления эмульгируюший свойств поверхностно-активных веществ пригодных для вытеснения сырой нефти из недр. В связи с этим, выяснение влияние типа и относительного содержания детергента, а также соотношения фаз на свойства эмульсий. Использовались 4-этокси-нонилфенол-слуъфонат в качестве анионного и нонилфенолы, с разным количеством этокси групп, в качестве неионных поверхнозтноактивных веществ.