

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

Behaviour of emulsions at elevated temperatures, and emulsification of crude oil fractions

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The investigations were focussed on the determination of the stability and rheological properties of emulsions prepared from natural crude oil and its fractions, using ion-free water and aqueous tenside solutions. The effects of temperature on the stability and rheological properties of the emulsions were tested in the presence of tensides and in surfactant-free systems.

The experimental results permit the conclusion that with increasing temperature the originally plastic emulsion first assumes pseudoplastic properties, and later Newtonian flow behaviour. The change in the rheological properties is attributed to the paraffin crystals present at low temperature in Algyő-2 crude oil, which also stabilize the emulsion structure. In the presence of non-ionic tensides, the oil external emulsions have a complex nature [O/W/O type], and demulsify readily at elevated temperatures.

The emulsification of the crude oil fractions indicates that asphaltenes not only stabilize the tenside-free emulsions, but play a decisive role in shaping the rheological properties as well. No clear-cut relation was found between the interfacial tension and the stability of the emulsions, whereas it is probable that the interfacial rheological properties (viscosity, elasticity, film-forming ability) can be correlated with the spontaneous demulsification.

Introduction

In part I [1], the emulsion-forming abilities of surfactants to be applied in enhanced oil recovery were investigated at constant temperature (363 K). However, in order to clarify the properties of emulsions that may be formed under reservoir conditions, it was necessary to study how the stabilities and viscosities of emulsions change when the temperature is increased. The effect of temperature is also important when the crude oil is brought to the surface in the form of an emulsion, and the latter has to be demulsified. Moreover, from the experimental findings outlined in the first paper, it seemed unavoidable to determine which of the crude oil components, presumably the natural surfactant, basically shapes the rheological properties of the emulsions.

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Experimental

The crude oil and surfactants used in the experiments were the same as described earlier [1]. Separation of the crude oil into its fractions was carried out as follows: After distillation up to 473 K under atmospheric conditions, the atmospheric residue was subjected to vacuum distillation at 53.32 Pa and 523 K. These two fractions together represented the oil phase designated T. Addition of *n*-pentane resulted in the precipitation of the asphaltenes from the vacuum residue. The *n*-pentane-free maltheine was then adsorbed on a Kieselgel, from which the resins and the residual fractions were extracted with benzene and methanol.

In the fractions obtained, the following phases maintained the concentrations of the different components at the same level as in the original crude oil.

- phase a: T + 0.3 w. % resin,
- phase b: T + 3.5 w. % asphaltene,
- phase c: T + 0.3 w. % resin + 3.5 w. % asphaltene,
- phase d: T + 10.7 w. % asphaltene-free and resin-free residue,
- phase e: T + resin-free fraction (3.5 w. % asphaltene + 10.7 w. % asphaltene-free and resin-free residue),
- phase f: synthetic (reconstituted) crude oil.

The interfacial tension between the oil and distilled water was determined by the pendent drop method. A Contraves Low Shear 30 viscometer was used to study the interfacial rheological properties of the two-phase system [2].

Results and discussion

1. Effects of temperature on stabilities and rheological properties of emulsions in tenside-free systems

In this test series, the emulsions contained equal phase volumes of crude oil and ion-free water. The dispersed systems were prepared at a given temperature and maintained under these circumstances for 24 hours.

It was observed that all emulsions were of W/O type, independently of temperature, and their thermal treatment did not lead to any phase separation. Notwithstanding this, the emulsions cannot be regarded unequivocally as stable ones. At room temperature, the significant difference in viscosity between the two liquid phases tends to prevent the disperse portion from separating from the system. The emulsified drops are stabilized by the natural emulsifiers present in the crude oil, and the emulsion structure is stabilized by crystals of the high molecular weight paraffins still in solid form at 298 K. As the temperature was elevated to 323, 348 and 363 K, the increase in the drop size and their settling could be observed visually. The reduction in oil viscosity with increasing temperature made it possible for the drops to settle, resulting in a lower distribution stability of the system. As the temperature rises, the solid paraffin particles melt, and they cease to have any role whatever in the apparent stabilization of the emulsion.

The flow curves measured at constant temperature after thermal treatment are illustrated in Fig. 1. It is clear that any shift in temperature leads to a change in the

flow behaviour of the emulsions. The dispersed system, that exhibits plastic properties at room temperature, becomes pseudoplastic at 323 and 348 K, and behaves essentially as a Newtonian liquid at 363 K. At the same time, a considerable change also takes place in the plastic viscosity and the Bingham yield value, as shown in Fig. 2.

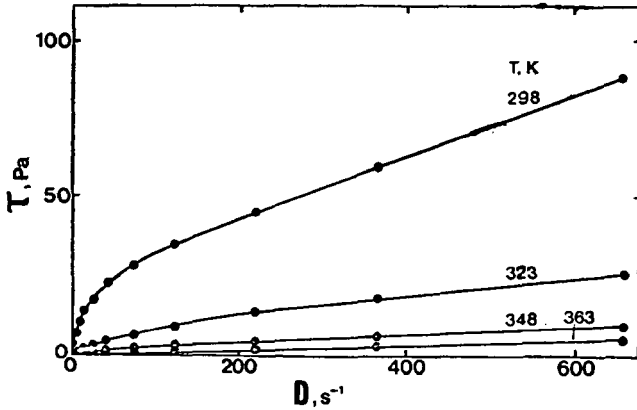


Fig. 1. Ascending legs of flow curves at 298, 323, 348 and 364 K, for emulsions containing 50 vol. % crude oil and 50 vol. % distilled water

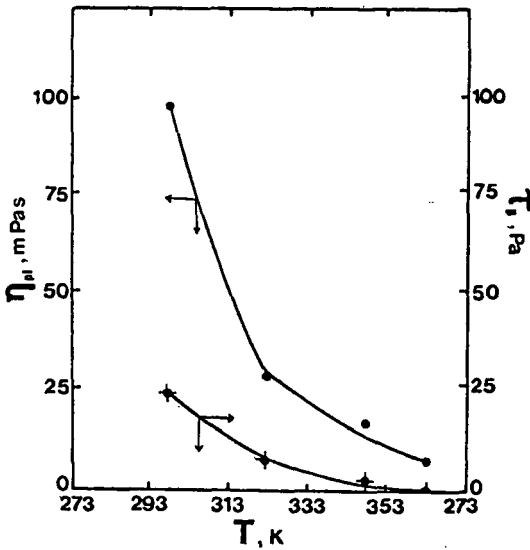


Fig. 2. Bingham yield value (τ_B) and plastic viscosity (η_{pl}) vs. temperature for emulsions of 50 vol. % crude oil and 50 vol. % distilled water

From Fig. 2, it may be stated that the greatest change in the emulsion viscosity is caused by raising the temperature from 298 K to 323 K. It is presumably, in this range that a large proportion of the long-chain paraffins melt and dissolve in the dispersion medium.

2. Effects of temperature on stabilities and rheological properties of emulsions containing tenside

Tensides containing 8 or 20 ethylene oxide groups were chosen as model compounds. The concentration of surfactant was selected so that an oil external emulsion formed in one case and a water external emulsion formed in the other when equal volumes of oil and water were mixed at 298 K [1]. Tenside solutions of 0.5 g dm^{-3} and 40 g dm^{-3} , from surfactants NPE_8 and NPE_{20} , respectively, were therefore used to produce an O/W emulsion at room temperature. The emulsions were prepared at the given temperature and allowed to stand for 24 hours under thermostated conditions, after which the flow curves were measured. The apparent viscosities obtained at different temperatures are shown in Figs 3 and 4.

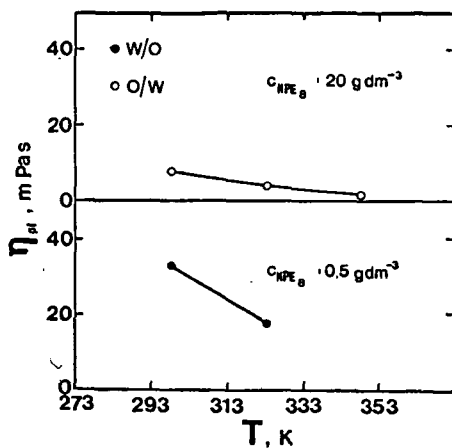


Fig. 3. Temperature-dependence of emulsions stabilized with tenside NPE_8 .

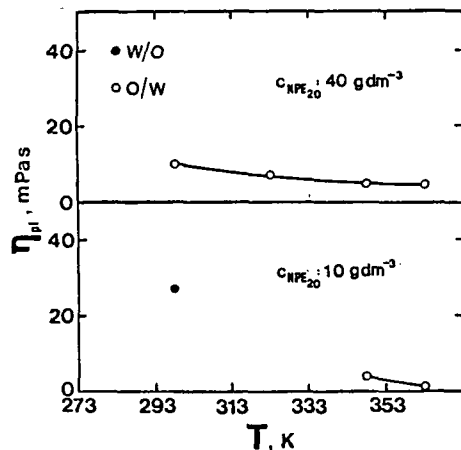


Fig. 4. Temperature-dependence of emulsions stabilized with tenside NPE_{20} .

It is obvious from Fig. 3 that on increase of the temperature by 25 K the viscosity decreased from 33 mPas to 17 mPas. On the other hand, the emulsions obtained at 348 and 363 K underwent full demulsification after 24 hours and they separated, in accordance with their initial composition, into 50 vol. % oil and 50 vol. % aqueous phase.

When the emulsions were prepared with a solution having a tenside concentration of 20 g dm^{-3} , each of them proved to be of the O/W type. It is apparent from Fig. 3 that the viscosity of the emulsion is already below 10 mPas at 298 K, and it diminishes to 2 mPas if the temperature is increased to 348 K. After thermal treat-

ment for 24 hours, separation of neither the dispersed portion nor the dispersion medium could be observed up to 348 K. On the other hand, at 363 K (the highest temperature used) the emulsion demulsified into 3 phases, with formation of an O/W emulsion in the middle zone. Its volume comprised 23% of that of the initial emulsion.

SHINODA and ARAI [3] have studied in detail the relationship between the cloud point and the phase inversion temperature. On the basis of their experimental results it can be stated that for a given tenside the phase inversion temperature depends to a large extent on the composition of the oil phase. It also depends on the oil phase whether the phase inversion temperature is lower or higher than the cloud point. For an oil phase abundant in aromatic compounds, the phase inversion temperature is usually lower than the cloud point, while it tends to exceed the latter in the cases of normal and cycloparaffins. For a given tenside (for a given cloud point), the phase inversion temperature increases if a compound containing a longer hydrocarbon chain is present in the oil phase. This may explain why a water external emulsion occurs well above the cloud point (318 K) when NPE_8 is used, while the O/W emulsion becomes unstable at 348 K.

According to SHINODA and SAGITANI [4], the stability of the O/W emulsion drops against coalescence is greatest if the storage temperature is 20 to 55 degrees lower than the inversion temperature. Thus, the value of 363 K may be near the phase inversion temperature above which a W/O emulsion may already occur.

The emulsions prepared with 10 g dm^{-3} NPE_{20} solution (Fig. 4) are of W/O type at room temperature and 323 K, and of O/W type at 348 and 363 K. The viscosity of an emulsion stored at 298 K for 24 hours does not differ significantly from that of an emulsion prepared with 0.5 g dm^{-3} NPE_8 (Fig. 3). At higher temperatures, the viscosity of water external emulsions is small, amounting to merely a few mPas.

After thermal treatment at 323 K, the originally W/O emulsions separated into 3 phases. The amount of the O/W emulsion between the boundaries of the oil and aqueous phases is about 5% of the initial volume. This water external emulsion can only be a result of the demulsification of the initially complex O/W/O type system.

After 24 hours, the O/W emulsions thermally treated at 348 and 363 K showed diffuse opalescence. The emulsions prepared with 40 g dm^{-3} NPE_{20} were of the O/W type at any temperature. At room temperature, the viscosity level was about 10 mPas, and it decreased only slightly as the temperature increased. It could also be stated that, on standing at a given temperature, the stability of the emulsified drops against coalescence was high and neither the dispersion medium nor the dispersed phase separated from the system as a discrete liquid. At the same time, the distribution stability of the emulsions is low (as usual other O/W emulsions) and they show diffuse distribution at any temperature.

It seems a contradiction that when these non-ionic tensides are used, a W/O emulsion can be produced at low temperatures, and an O/W emulsion at higher temperatures, whereas just the opposite might be expected on the basis of theoretical considerations. An explanation of this question must be sought in the composition of the hydrocarbon phase. According to the experimental results of SHINODA and ARAI [3], the phase inversion occurs at a temperature higher than the cloud point if the oil phase contains mainly paraffins. Typically, Algy δ -2 crude oil is rich in paraffins of different chain lengths [5], *i.e.* in components which may increase the phase inversion temperature above the cloud point. It can be seen from the data in Table I that up to

373 K no opalescence of the aqueous solution of tenside NPE₂₀ takes place. Thus, the phase inversion temperature should be higher than 373 K. The experimental fact that a W/O emulsion forms at low tenside concentrations and temperatures, and an O/W emulsion at higher temperatures [6], is not connected directly with the phase inversion that might be expected from the change in the HLB of non-ionic tensides due to increased temperature. The alteration in emulsion character observed as a result of increased tenside concentration and that effected by temperature may possibly be explained by the chemical nature of compounds present in Algyδ-2 crude which stabilize the oil external system. This possible interaction leads to destabilization of the initial emulsion. At lower temperature, the solid particles also take part in the apparent stabilization of the dispersed system. They melt when the temperature increases, and a stable emulsion can be formed only if a sufficient amount of tenside is present in the system; on the other hand, the emulsion demulsifies if this is not the case.

3. Stability of emulsion prepared from crude oil fractions

The different phases (T, a—e, listed earlier) were mixed with an equal volume of distilled water at 298 K. No stable emulsion was obtained by emulsifying phase T, and separation of the phases occurred immediately on preparation. The emulsification of phase e(T+resins) did not result in a stable emulsion either, and breaking of the system started even at room temperature. At 323 K and on standing over 1 hour, 4% of the initial volume remained in emulsion form. The respective values for 348 and 363 K were 2 and 1%. Addition of asphaltenes to phase T (phase b) led to an extremely stable emulsion, with neither the dispersed portion nor the dispersion medium separating out of the system under identical circumstances.

On emulsification of phase c (T+resins+asphaltenes), breaking of the emulsion could not be observed at room temperature. However, the dispersion medium began to separate at 323 K, and its volume amounted to 22% of the initial emulsion. It could also be observed that the drop size increased with rising temperature.

The emulsion was stabilized only slightly by the asphaltene-free and resin-free residue, and separation of the two phases became complete at 323 K. Emulsification of the resin-free phase (phase e) gave a stable emulsion. No increase in the water drop size was visible to the naked eye. At 363 K, after a standing time of 1 hour, oil separated from the emulsion, its volume amounting to 10% of the original volume of the emulsion. Emulsification of phase f (the reconstituted synthetic oil) gave a very stable emulsion, similar to that prepared from phase e; at 363 K, only oil separated from the emulsion, but its volume was less than 10% of the initial volume.

Previously, the interfacial tension was regarded as the factor playing the crucial role in emulsification and emulsion stability [7]. For instance, MARSZALL [8] suggests that a low interfacial tension is a necessary, but insufficient condition of stability. On the other hand, the studies of interfacial rheological properties revealed a relatively close correlation between the stability and viscosity of the emulsions. BOYD ET AL. [9] found that the stability depends highly on the elasticity of the rigid films formed at the water/oil interface. WASAN ET AL. [10] found that in systems with an ultralow interfacial viscosity the drop coalescence occurs very rapidly, *i.e.* the emulsions are unstable.

Table I

Characteristic interfacial tension, interfacial and plastic viscosity, and Bingham yield value for different oil/water systems

Hydrocarbon phase	σ $\times 10^{-3} \text{ N m}^{-1}$	η_s $\times 10^{-3} \text{ N s m}^{-1}$ 4 h, $D = 5.14 \text{ s}^{-1}$	η_{pt} $\times 10^{-3} \text{ N s m}^{-2}$	τ_B N m^{-2}
T	14.65	—	—	—
a	11.06	3.22	—	—
b	17.51	18.90	92.7	21.4
c	16.33	11.03	62.5	15.0
d	14.13	24.60	38.4	2.2
e	18.62	28.70	114.3	54.6
f	16.60	30.71	113.1	36.5
Crude oil	22.10	45.76	103.2	34.8

Of the interfacial film properties, interfacial tension and interfacial viscosity were measured at 298 K in a system composed of various crude oil fractions and distilled water. The build-up of an interfacial layer is a time-consuming process, which cannot be followed through the interfacial tension alone, as the latter comes into equilibrium after 10 to 20 minutes, regardless of the chemical composition of the oil phase (Fig. 5).

In the first column of Table I the equilibrium interfacial tensions are listed. Comparison of these data with those measured during the stability tests shows that the interfacial tension in the case of the most stable emulsions does not constitute the lowest value. The lowest interfacial tension was found for phase a, which forms a read-

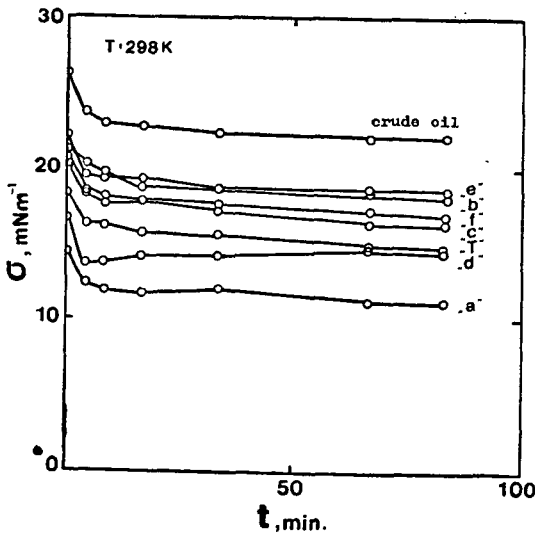


Fig. 5. Time-dependence of interfacial tension in oil/water system

ily breaking emulsion. However, it should be noted that certain crude components and compounds undergo autoxidation during the preparation of the different fractions, which leads to the formation of compounds active at the interfaces. The fact that the interfacial properties of the original crude and the "synthetic" (reconstituted) oils are different is attributed to this phenomenon.

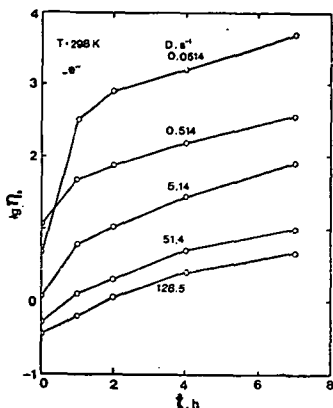


Fig. 6. Change of interfacial viscosity vs. shear rate in phase e/water system

Formation of the interfacial layer can be followed better through the change in the interfacial viscosity as a function of time. Figure 6 presents data on the viscosity of the interface between phase e and distilled water at different shear rates.

The shapes of the curves in Fig. 6 are similar to those obtained for the other fractions, *i.e.* the greatest change is measured within 1 hour, and the build-up of the interfacial layer continues even after 4 hours.

The characteristic interfacial viscosities measured after 4 hours and at $D=5.14 \text{ s}^{-1}$ are also included in Table I. Analysis of the data reveals a correlation between the interfacial viscosity and the properties of the emulsions. It is quite reasonable that the emulsion prepared from phase a, having an interfacial viscosity of merely 3.22×10^{-3} , is

unstable. However, a highly stable emulsion is formed in the asphaltene-containing system, where the interfacial viscosity is relatively high.

Unfortunately, we are faced with special experimental circumstances which hinder the establishment of a close correlation between the emulsion stability and the interfacial rheological properties. The problems stem from the fact that, when a rheometer is used in the rotation mode of operation, the highly elastic, rigid films formed at the interface in asphaltene-containing systems are usually ruptured at very low ($<0.1 \text{ s}^{-1}$) shear rate and therefore the values reported in Table I are probably far below the actual interfacial viscosities existing at a state of rest or at very low shear forces. Thus, it seems unavoidable to complement the present studies with oscillation rheometric measurements and to seek relationships between the emulsion stability and the elastic properties (strong modulus, shear rigidity, compliance, etc.).

4. Rheological properties of emulsions prepared from different crude oil fractions

The ascending leg of the rheograms for the emulsions containing oil phases of different compositions is shown in Fig. 7; the plastic viscosity and the Bingham yield values of the emulsions are listed in Table I.

It is obvious from the flow curves presented in the Figure that asphaltenes play a key role in the plasticity of the emulsions. If only the asphaltenes of the heavy cut are present in the oil phase of the emulsion (curve b), the plastic viscosity is reduced slightly and the yield value decreases to a greater extent than for the emulsion prepared from the original crude oil (Table I). The presence of resins besides the asphaltenes reduces the plasticity, while if only the resin is absent from the oil phase (curve e)

the flow curve over the entire range of measurement will run above the curve for the emulsion prepared from the initial crude and distilled water, whereas the Bingham yield value increases from 34.8 Pa to 54.6 Pa and the plastic viscosity from 103.2 to 114.3 mPa s. When neither resins nor asphaltenes are present in the oil phase (curve **d**), a drastic change takes place in the emulsion structure: adhesion forces scarcely exist between the dispersed drops, and the viscosity of the emulsion is 38.4 mPa s. If the oil from the various fractions is reconstituted and mixed with an equal volume of distilled water, an emulsion is obtained whose flow curve approximates fairly well to that of the emulsion prepared from the initial crude oil, but it runs above it for the reasons mentioned earlier.

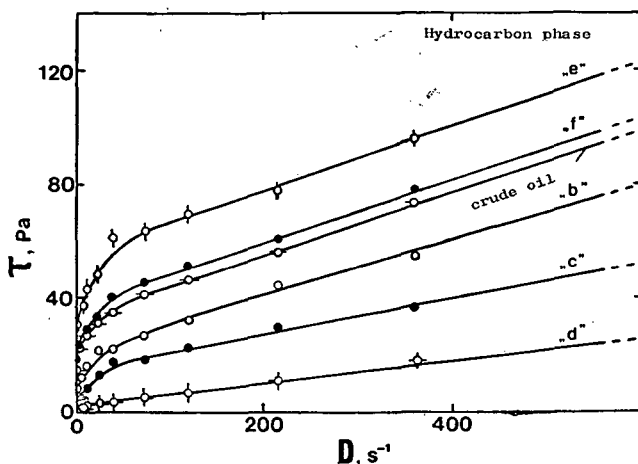


Fig. 7. Flow curves of different emulsions containing 50 vol. % hydrocarbon and 50 vol. % ion-free water

These experimental results agree with the literature observations [11—13]. Accordingly, of all the oil components, it is the asphaltenes that primarily stabilize natural crude oil-water systems. Asphaltenes are of basic importance not only in the stabilization of the emulsion, but also in determining its rheological properties. When the oil phase contains only asphaltene besides phase **T**, the flow curve for the emulsion best approaches that for the emulsion prepared from the original crude. The presence of resins definitely reduces the emulsion plasticity (curve **c**), whereas in their absence (curve **e**) it is possible to produce an emulsion having a higher plasticity and viscosity than those of the original emulsion.

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ИССЛЕДОВАНИЕ ЭМУЛЬСИЙ НЕФТИ В ВОДНЫХ РАСТВОРАХ НЕИОНОГЕННЫХ
 ПОВЕРХНОСТНО—АКТИВНЫХ ВЕЩЕСТВ, II. СВОЙСТВА ЭМУЛЬСИЙ ПРИ
 ПОВЫШЕННЫХ ТЕМПЕРАТУРАХ И ЭМУЛЬСИФИКАЦИЯ ФРАКЦИЙ НЕФТЫ

Б. Фелиан, Я. Балаж, Й. Лакатос-Сабо и И. Лакатос

Проведено изучение стабильности и реологических свойств эмульсии нефти и ее фракций образованных в воде и растворах поверхностно-активных веществ. Определено влияние температуры на указанные свойства эмульсий. Найдено, что асфальтены содержащиеся в нефти играют роль стабилизатора и важного фактора в определении реологических свойств в эмульсиях, приготовленных без поверхностно-активных веществ. Не найдено корреляции между поверхностным натяжением, поверхностной вязкостью и стабильностью эмульсий различных фракций нефти.