

The Effects of Anionic Surfactants on the Conductivity of a Water-in-Oil Emulsion in a Dielectric Hydrophobic Capillary

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Abstract—The effect of anionic surfactants on the conductivity of a water-in-crude oil emulsion in a laminar flow inside a dielectric hydrophobic capillary is experimentally investigated in an alternating electric field with strengths ranging from 4 to 10 kV/cm and a frequency of 50 Hz. Conductivity is analyzed as a function of aqueous phase concentration, electric field strength, and surfactant concentration in the dispersed phase.

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Earlier [1], it was briefly reported that the conductivity of a water-in-oil emulsion in a strong electric field decreases drastically when an anionic surfactant (AS) is present in its aqueous phase. This effect is of not only scientific, but also of practical interest, as it can be employed to control the electrical properties of emulsions subjected to electric fields, particularly in the course of crude oil electrical deemulsification [2].

This paper describes the results of a vast series of experiments aimed at a more detailed study of the influence of AS and electric field strength on the conductivity of a water-in-crude oil emulsion in a flow.

The experimental procedure was described in detail elsewhere [1]. It should be specified that only sodium alkylbenzenesulfonates of the formula $C_nH_{2n+1}C_6H_4SO_3Na$ ($n = 10–13$) based on n paraffins were used as ASes; the measurements were performed at 295 K. The regime selected for the preparation of the artificial water-in-crude oil emulsion ensured the same initial dispersity, i.e., the average droplet diameter of the aqueous phase was $\approx 10 \mu\text{m}$ in all of the experiments.

Note that the conductivity of water-in-oil emulsions is rather difficult to measure in strong electric fields, mainly because of the formation of continuous conducting structures composed of dispersed phase droplets, of so-called chains, which utterly distort the measurement results. This process is uncontrolled under usual conditions. In order to avoid the effects of the aforementioned factor, measurements were carried out in a special flow through cell (Fig. 1), in which a hydrophobic capillary (3) (fluoroplastic) with an internal diameter of 1.5 mm was placed between high voltage electrodes (1, 2). The emulsion under examination was pumped through the measuring cell at a constant flow rate in the capillary (0.25 m/s) corresponding to the laminar regime.

As was experimentally found earlier [3], no continuous chains are formed in an emulsion moving through such a capillary at a dispersed phase concentration below 9–10 vol %, while water droplets intensely coalesce. The hydrophobicity of the capillary prevents the formation of a conducting water film on its walls, the presence of which could distort the measurement results.

An analysis of the results obtained suggests that, given that the other conditions are equal, the intensity and the character of AS effect on the emulsion conductivity depend strongly on the concentration of the dispersed aqueous phase. For example, in the examined range of AS concentrations (in the aqueous phase), the limits of variations in the conductivity G of an emulsion containing a 3 vol % dispersed phase are shifted, at most, by 35% and 63% toward higher and lower values, respectively, relative to the conductivity G_0 of an AS-free emulsion (Fig. 2a). At an aqueous phase content of 10 vol % and in the same AS concentration range, the conductivity of the emulsion subjected to an external electric field with a strength of $E_0 = 4 \text{ kV/cm}$ changes by a factor of 40, in stronger fields, G increases even more rapidly, thus causing the electrical breakdown of the emulsion (Fig. 2c). The strongest and most specific variations in the conductivity of an emulsion with an AS concentration in its aqueous phase is observed when the content of the latter is 5% (Fig. 2b). In this case, the G value decreases by a factor of 180.

The pattern of the dependence of G on the AS concentration (C_{thr}) also strongly changes with the aqueous phase concentration. This dependence has the simplest character at an aqueous phase concentration of 10%; as $G = f(C_{\text{thr}})$ rises, the conductivity monotonically increases with acceleration. At lower dispersed phase concentrations, dependences $G = f(C_{\text{thr}})$ have a more

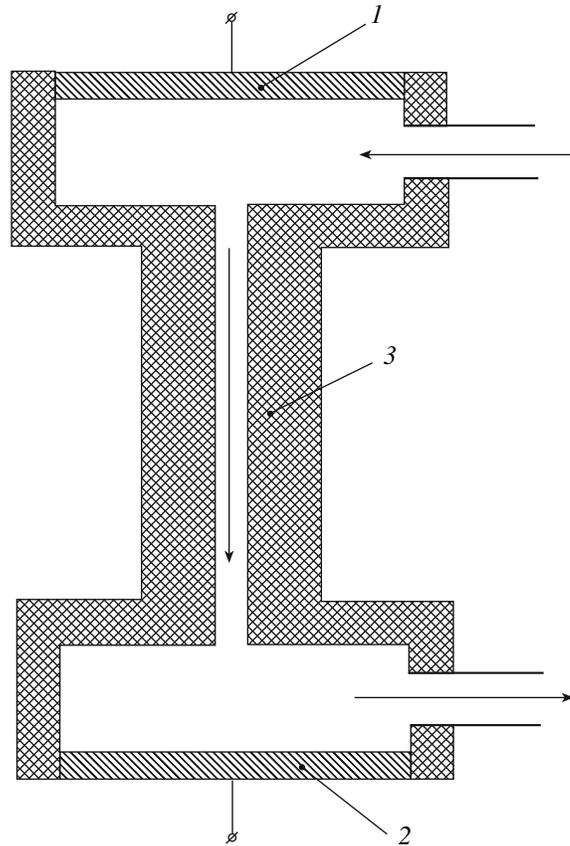


Fig. 1. Schematic representation of the flow through cell: (1, 2) high voltage electrodes and (3) dielectric hydrophobic capillary.

complex two-extreme character. A comparison of the curves in Fig. 2 allows us to follow the evolution of the character of the emulsion conductivity–AS concentration dependence with a rise in the content of the dispersed aqueous phase.

In our opinion, the conductivity behavior at aqueous phase concentrations is the most interesting in the vicinity of 5%, as this is the region in which G values depend quite strongly on the AS concentration. As can be seen from Fig. 2b, the emulsion conductivity decreases dramatically when the AS concentration in the dispersed phase increases from 0.5 to 1%. The multiplicity of a reduction in G relative to the conductivity of an AS-free emulsion, other conditions being equal, depends on the external electric field strength, with the multiplicity changing from 66 to 180 at $E_0 = 4$ and 10 kV/cm, respectively. It is significant that at sufficiently high electric field strengths, the conductivity of a 5% emulsion with an AS concentration of 1% coincides, within the measurement error ($\pm 1.5\%$), with the conductivity of water-free crude oil under the same conditions.

Let us turn now to the Wagner theory of dilute disperse systems [4]. According to this theory, when the conductivity χ_w of a dispersed phase is much higher

than that of the dispersion medium χ_o , the following equation is valid:

$$\chi = \chi_o \frac{1 + 2\Phi}{1 - \Phi}, \quad (1)$$

where Φ is the volume fraction of the dispersed phase.

For the investigated water-in-oil emulsion, the condition $\chi_o \ll \chi_w$ is strictly satisfied ($\chi_o = 6.3 \times 10^{-8}$ S/m and $\chi_w = 1.4 \times 10^{-4}$ S/m) and the condition $\Phi < 0.09$ corresponds to a dilute system. For the conductivity of a 5% emulsion ($\Phi = 0.05$), the calculation by Eq. (1) yields $\chi = 1.16\chi_o$. Since the parameters of the measuring cell remained unchanged throughout the course of the experiments, Eq. (1) may be rewritten based on the conductivities of the emulsion G and crude oil G_0 as follows:

$$G = G_0 \frac{1 + 2\Phi}{1 - \Phi}. \quad (2)$$

Thus, the conductivity of the emulsion with $\Phi = 0.05$ is expressed via the conductivity of its dispersion medium (crude oil) as $G = 1.16G_0$; that is, it is higher than the latter by 16%. At the same time, in an external electric field with a strength of $E_0 = 10$ kV/cm, the experimentally measured conductivity for a 5% emulsion, the dispersed phase of which contained 1% AS, is higher than

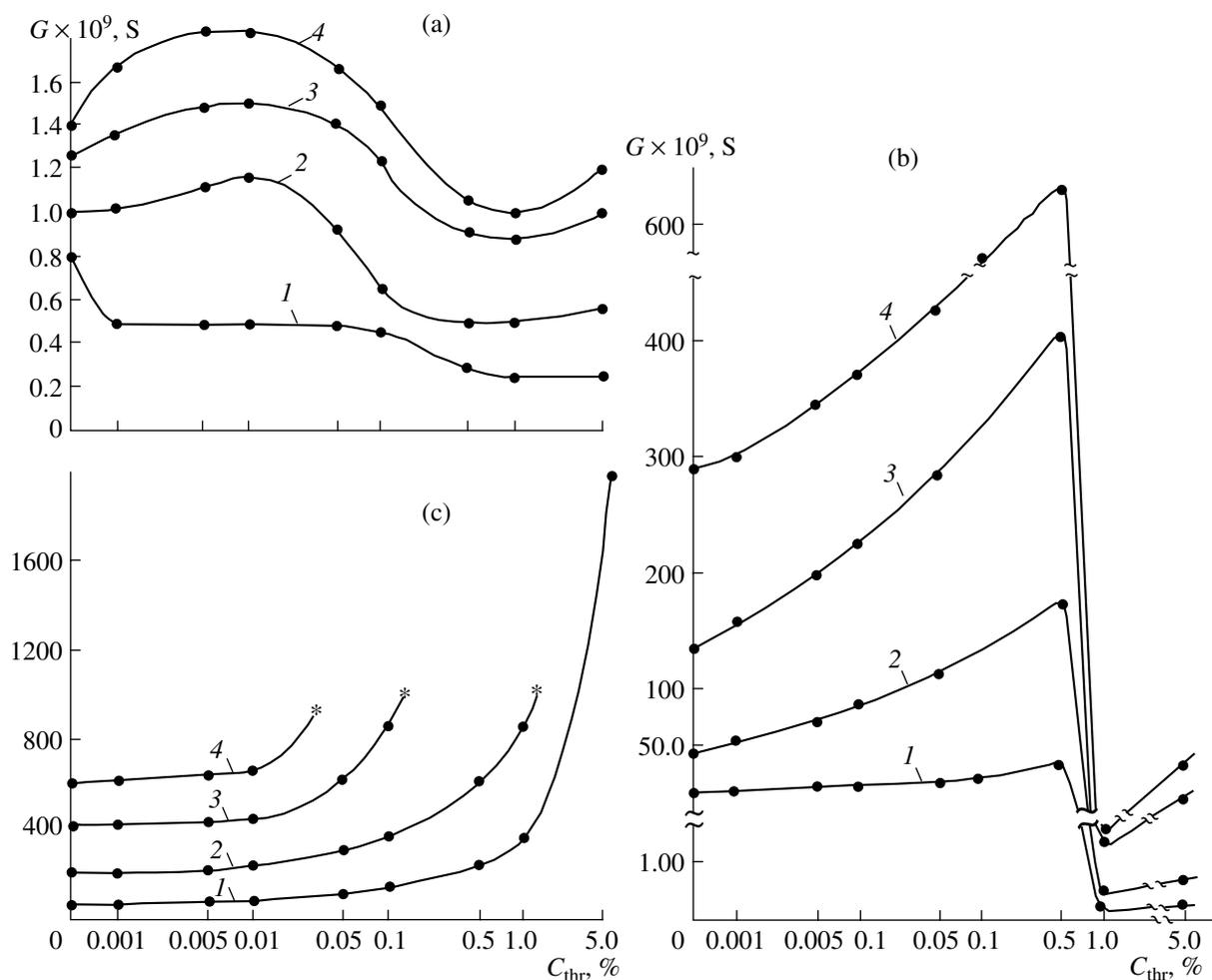


Fig. 2. Emulsion conductivity as a function of AS concentration in an aqueous phase at different external electric field strengths: (1) 4, (2) 6, (3) 8, and (4) 10 kV/cm. The water concentration in the emulsions is (a) 3, (b) 5, and (c) 10%.

that of water-free crude oil by 19%, other conditions being equal. With allowance for the fact that the conductivity of crude oil in strong electric fields increases somewhat with the field strength [5], the theoretical and observed values coincide with a good accuracy.

In general, an increase in the conductivity of a dispersion medium resulting from the incorporation of dispersed phase particles may be explained by the following two factors: the partial replacement of the medium volume by particles with higher conductivities, and, the involvement of the particles in a charge transfer in an external electric field [6]. Taking into account the fact that the experiments were performed in an alternating electric field and at quite low concentrations of dispersed phase droplets, the latter factor may be ignored. The decrease in the conductivity of the water-in-oil emulsion under the aforementioned conditions may then be explained by the exclusion of the contribution of dispersed phase droplets to current carrying. In other words, the water-in-oil emulsion behaves as a uniform low conducting liquid rather than

a disperse system with a conducting dispersed phase. This fact may be confirmed by an analysis of the plots in Fig. 3, where the experimental dependences of $\ln G$ on the external electric field strength is illustrated for 5% emulsions with different AS concentrations in the dispersed phase. At an AS concentration of 1%, the $\ln G = f(E_0)$ plot qualitatively changes in the appearance of an inflection point and a linear region within it. Thus, when the external electric field is stronger than 7 kV/cm, the $G = f(E_0)$ dependence obeys the exponential law. The same phenomenon is also observed for an emulsion whose dispersion phase contains 5% AS, the only difference being that the dependence acquires an exponential character at $E_0 > 9$ kV/cm and that the linear region of the plot has another slope.

It was experimentally established [5] that the conductivity of water-free crude oils depends exponentially on the external electric field strength when E_0 is higher than some threshold value, E_{thr} . In particular, an empirical equation was obtained for the $\chi(E_0)$ dependence at a constant temperature [5].

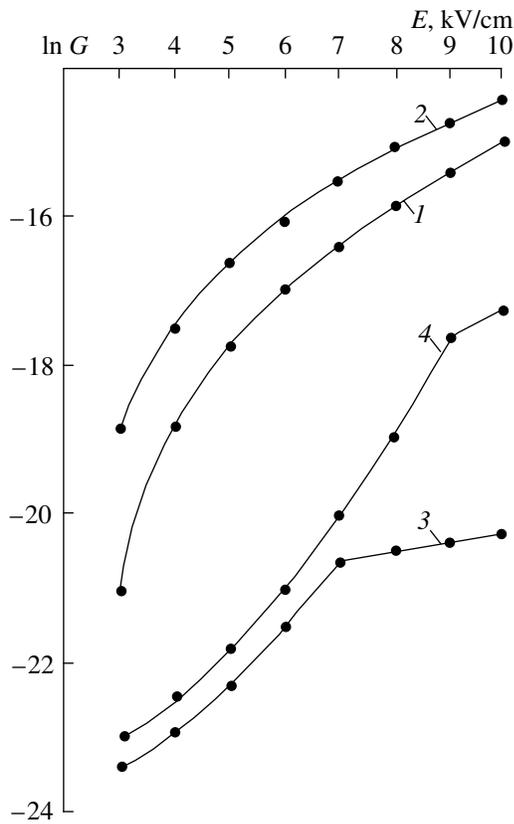


Fig. 3. Electric conductivity of a 5% emulsion as a function of external electric field strength at different AS concentrations in the aqueous phase: (1) 0.001, (2) 0.1, (3) 1.0, and (4) 5.0%.

$$\chi(E_0) = \chi_0 e^{\alpha(E_0 - E_{thr})d}, \quad (3)$$

where χ_0 is the conductivity of crude oil at a fixed temperature, d is the distance between electrodes, and α is a coefficient characterizing the rate of a rise in $\chi(E_0)$ with variations in field strength E_0 . Coefficient α is interpreted as an intensity ratio for the generation and recombination of free electrons.

In our experiments, the distance between the electrodes remained unchanged, while the threshold strength and coefficient α depended on the AS concentration in the dispersed phase of an emulsion at $C_{thr} > 1\%$, with E_{thr} and α increasing with the concentration.

As the studied emulsion has a pronounced interface, it seems to be reasonable to assume that in a strong field, the abnormal behavior of the conductivity in the presence of an AS is determined by the processes carried out at the interface and in the dispersion medium. Indeed, the experimental studies [7] demonstrated that the pattern of potential distribution at the water–crude oil interface strongly depends on AS concentration in the aqueous phase, with the interfacial potential difference drastically falling at AS concentrations of $\approx 1\%$.

Additionally, the effects caused by the polarization of the electrical double layers of dispersed phase droplets in strong electric fields [8] may contribute to the phenomenon under consideration.

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