Kinetics of the Establishment of Effective Conductivity in an Oil–Water System in the Presence of Nonionic Surfactants

A. A. Yunusov[a] and N. N. Khafizov[b]

[a] *Joint-Stock Company Oil Equipment and Technology, ZAO Neftekh, a/ya 96, Kazan, 420095 Tatarstan, Russia*
[b] *Kazan State Technological University, ul. Karla Marksa 68, Kazan, 420015 Tatarstan, Russia*
Received June 15, 2007

Abstract—The kinetics of the establishment of the effective conductivity in an oil–water system with a flat interface after the phases are brought to contact is experimentally found and investigated. The influence of water- and oil-soluble nonionic surfactants on the pattern of the kinetic curves and the degree of variation in the conductivity of the system with time is studied within a range of 30 s–330 min.

INTRODUCTION

According to the current concepts, the scheme of the coalescence mechanism of water emulsified in oil under the action of an external electric field comprises the following stages: deformation of spherical water droplets into ellipsoids of revolution, their approch under the action of the electrostatic dipole–dipole attraction forces, the breakdown of the adsorption shells of the droplets and interparticle films of the dispersion medium, the formation of thin channels, and the drops' fusion [1–3].

The enlargement of droplets of mineralized deposit water in the course of oil dehydration or mixed deposit and sweet waters during oil demineralization is a condition necessary to reach a required extent of oil dehydration and demineralization in the course of subsequent gravity separation of water and salts from oil being prepared for further processing. At the same time, it has been shown that the approach of emulsified water droplets polarized in an electric field does not always end in their coalescence. The latter process may be hindered by the contact–disconnection charging of droplets, which consists in the contact or contact-free charge reversal of droplets, their charging with similar charges, and generation of electrostatic repulsion forces causing the droplets to move away from one another [4–7]. It is obvious that the intensity of this effect must be dependent on the electrophysical properties of both adsorption interfacial layers at dispersed phase droplet–dispersion medium interfaces and interdroplet oil, that is, on the conductivity and electric strength of these objects.

Currently, various chemical reagents (surface-active demulsifiers, inhibitors of corrosion and deposition of paraffins and salts, viscosity-decreasing agents, bactericides, etc.) are widely used in the processes of oil extraction, transport, and preparation for processing. Earlier, we investigated the influence of surface-active demulsifiers on volume conductivity of sweet (distilled) water, water containing dissolved inorganic salts, and dehydrated oil [8–10]. However, taking into account the extremely important contribution of nonionic surface-active demulsifiers to the macroscopic properties of disperse systems and processes occurring at dispersed phase–dispersion medium interfaces, the experimental study of their effect (at the first stage) on the conductivity of oil–water systems as a whole is of undoubted interest. On the other hand, the analysis of the experimental kinetic studies of the formation of adsorption shells on water droplets emulsified in oil and adsorption films at flat oil–water interfaces employing variations in their mechanical strength with time [11–15], reasonably suggests that the electrophysical properties of such systems must undergo some evolution after the phases are brought to contact. In this work, we attempted to reveal this kinetics and to determine its regularities and quantitative characteristics.

EXPERIMENTAL

The object of the study was an oil–water system with a flat interface. The volume conductivities of distilled water and dehydrated oil at 295 K were 2.12×10^{-4} and 4.73×10^{-7} S/m, respectively.

The applied laboratory setup comprised a measuring cell, a B5-46 stabilized source of direct current, a Shch 301 combined digital instrument, a current amplifier, a V7-40/5 universal digital voltmeter, and a liquid thermostat. All current-carrying elements of the setup were reliably screened, and the screens were grounded. Depending on the goal of an experiment, examined systems were prepared in the following ways. In the experiments using water-soluble nonionic surfactants
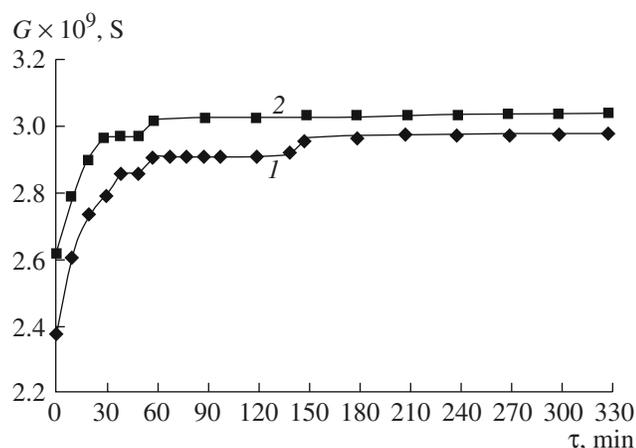
Fig. 1. Kinetics of f EC in a water–oil solution of Disolvan-4490 ONS system at concentrations of (*1*) 10^{-4} and (*2*) $10^{-1}\%$.

Fig. 2. Kinetics of EC in an oil–aqueous solution of Progalit NM 20/40 WNS system at concentrations of (*1*) 10^{-4} and (*2*) $10^{-1}\%$.

Fig. 3. Kinetics of EC in an aqueous solution of Disolvan-4411 WNS–oil solution of Demulfer R-11 ONS system at the following concentrations: (*1*) $10^{-4}\%$ WNS in water and ONS in oil and (*2*)$10^{-1}\%$ WNS in water and ONS in oil.

(WNSs), their solutions were prepared with preset concentrations and calculated volumes were poured into a thermostated cylindrical cell made of F-4 fluoroplastic and equipped with plane-parallel horizontal polished electrodes made of stainless steel. After air bubbles were removed from the surface of the solution and internal walls of the cell, preset volume of oil was carefully (along a glass plate) poured into the cell, the cover of the cell was screwed on, and the first measurement was performed over 10 s. In the experiments with oil-soluble nonionic surfactants (ONSs), oil solutions of ONSs were deposited onto an aqueous phase in the same way.

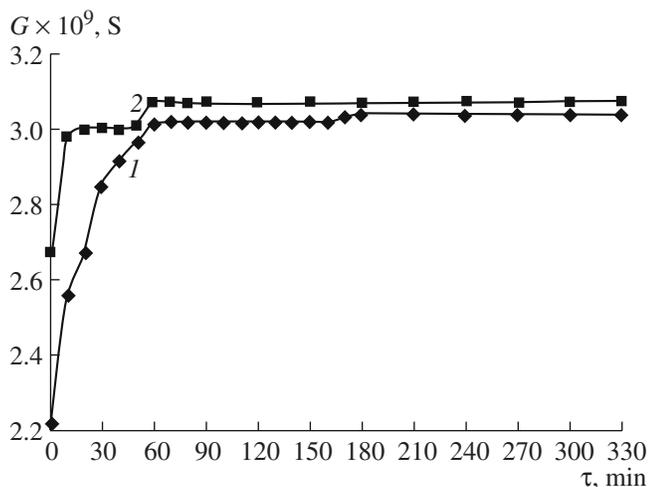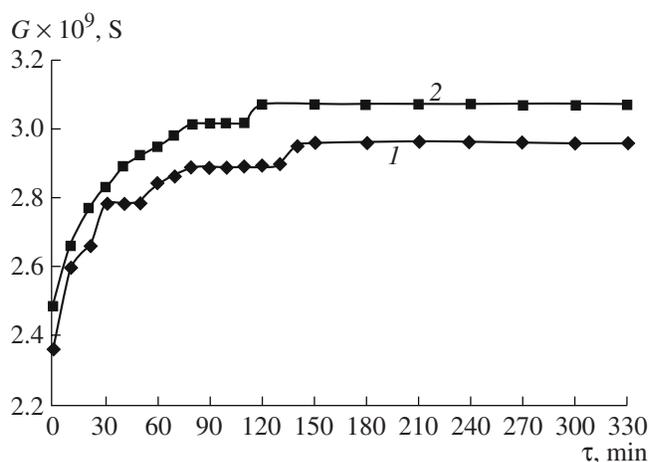Operating solutions with preset concentrations were prepared under moderate mechanical stirring for 10 min, and then, prior to placing them into the cell, they were thermostated at 295 K for 1 h to achieve diffusion equilibrium.

Employing precise feeders, we ensured a preset level of the interface in the interelectrode space (with an error of no more than 0.2 μm). The maximum absolute error in the direct current measurement at the operating limit equal to 10 nA was ±0.2 nA, and that of the V7-40/5 voltmeter at the limit of voltage measurement equal to 2 V was not larger than ±1.0 mV.

In order to exclude the distorting influence of the examined system electrocleaning and changes in the parameters of the electrical double layer (EDL) at the interface, the measurements were carried out at a low constant voltage of 1.7 V, which corresponded to an average strength of the external field in the interelectrode space of as low as 1.4×10^3 V/m. In the intervals between the measurements, a switching unit automatically switched off the voltage at the cell electrodes and short-circuited them. The cell was thermostated to maintain a preset temperature with an accuracy of 0.01 K in the course of an experiment.

Depending on the reproducibility, each experiment was repeated 3–5 times and the results were averaged.

RESULTS AND DISCUSSION

The measurement results are partly exemplified in a graphical form in Figs. 1–4. The experimental data are not presented for a number of other surfactants, because the kinetic curves are qualitatively close to those illustrated in Figs. 1–3 and demonstrate only some quantitative differences. Even a superficial analysis of the graphical data enables us to state that, in all of the cases in question, the equivalent conductivity (EC) of the oil–
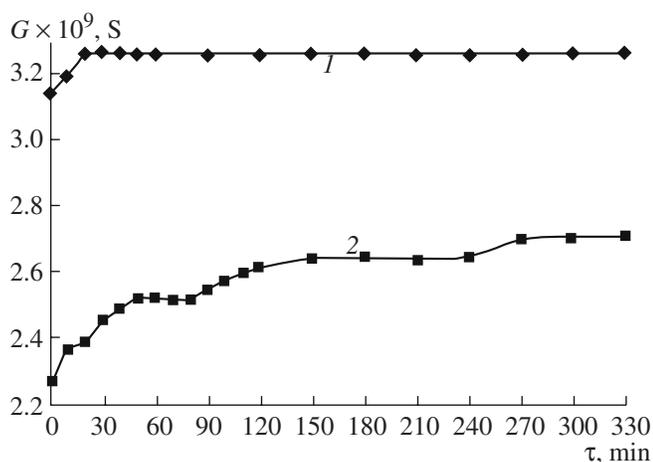
Fig. 4. Results of preliminary experiments using (*1*) an oil with an increased content of mechanical impurities–water system and (*2*) a 0.2% aqueous sodium chloride solution–oil solution of Disolvan-4490 ONS system with an ONS concentration of $10^{-2}\%$.

Fig. 5. Equivalent electrical scheme of the system.

water system has distinct kineties both in the presence of WNS or ONS in one or both contacting phases and in their absence. It is of interest that the times elapsed before EC acquires a constant value and the features of kinetic curves $G = f(\tau)$ are similar to these characteristics of the kinetic curves describing an increase in the mechanical strength of the interfacial adsorption films [13].

In order to analyze the obtained data in more detail, we should consider the following aspects. In general, the equivalent electrical circuit of the object under examination is a series-parallel RC chain (Fig. 5), where R and C units are the resistances and the capacities of capacitors with leakages corresponding to (*1*) a near-electrode layer in the oil phase, (*2*) the oil phase, (*3*) an interfacial layer (EDL) at the oil–water boundary (strictly speaking, a doubled layer [16]), (*4*) the aqueous phase, and (*5*) a near-electrode layer in the aqueous phase, respectively. However, as the measurements were performed at a constant voltage and the current was recorded in a steady-state regime (the time of the measurement was certainly much longer than the duration of charging capacitors $C_1–C_5$), the aforementioned capacities may be excluded from the consideration to take into account only the resistances.

The results obtained indicate that the range of relative variations in the system conductivity $(G - G_0)/G_0$ is rather wide and, depending on the nature and the properties of the nonionic surfactants under consideration, amounts to 16–52.6% (here, G is the steady-state maximum conductivity and G_0 is the initial conductivity value measured 60 s after the phases are brought to contact). In this situation, we should try to estimate the contribution of elements $R_1–R_5$ to the EC kinetics in the system. The relation between the conductivities of the
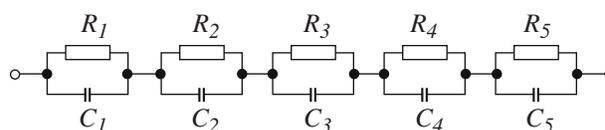
aqueous and oil phases is such that the resistance of the latter is 448-fold higher than that of the former. Thus, with allowance for the stipulation concerning capacitances $C_1–C_5$, in the circuit presented in Fig. 5, only R_1, R_2, and R_3 units may be (to different extents) rate-limiting, while any, including multiple, changes in the conductivity of the aqueous phase cannot have a measurable effect on the EC of the system as a whole.

Let us qualitatively assess possible contributions of likely factors to the mechanism of the observed kinetics. The contribution of the polarization of the electrode that is in contact with oil may be excluded for the following reasons. First, its polarization takes characteristic time $\tau_0 = \varepsilon_0\varepsilon/\chi$ [18], where ε and χ are the permittivity and conductivity of the medium, respectively, and ε_0 is the electric constant. For the oil phase, the calculation yields $\tau_0 = 4.0 \times 10^{-5}$ s. It is absolutely clear that this value is much smaller than the real duration of an act of the measurement and, all the more, the duration of the changes of the conductivity in the system. Second, in order to minimize the polarization effect [19, 20], the current density in the system was no higher than a negligibly small value of 3.1×10^{-10} A/cm^2.

As was found previously [8–10], the incorporation of colloidal nonionic surfactants (NSs) into oil somewhat changes its conductivity; however, the relative increase in the conductivity at NS concentrations of $10^{-4} – 10^{-1}\%$ and a temperature of 295 K is no higher than 5–6%. Moreover, the concentration dependence of oil conductivity has a complex nonmonotonic pattern. Thus, taking into account the preparation conditions of the operating solutions under mechanical stirring followed by thermostating for 60 min, there are, in our opinion, no reasons to assume that the volume conductivity of the oil phase (and, consequently, resistance R_2), after it is placed into the measuring cell, may noticeably vary with time as a result of NS diffusion in the oil phase.

We may easily ignore variations in ONS concentration in oil due to its adsorption at the interface, because, at the actual interfacial area of 2.83×10^{-3} m^2, the specific interfacial area of the examined system is negligibly small and amounts to only 1.4×10^{-5} m^2/cm^3.

Another factor, which can theoretically influence the observed kinetics, may be diffusion of surfactants through the interface and the dissolution of ONSs in water and WNSs in oil. According to producer informa-

tion, Progalit NM 20/40 WNS is partly soluble in aromatic hydrocarbons and commercial Disolvan 4411 WNS is miscible with oil. Demulfer R-11 ONS is partly soluble in water, while Disolvan-4490 is insoluble. However, with allowance for the fact that the conductivity of the aqueous phase is not the limiting factor in the system in question and that the conductivity of the oil phase increases by no more than 5–6% at the temperature of the experiments even when NSs are directly incorporated in it under vigorous stirring, the observed kinetics cannot be explained by the effect of the aforementioned factor alone, although this explanation would be the simplest and understandable.

On the other hand, we should remember that commercial nonionic surfactant-active demulsifiers (50–65% active substances in corresponding solvents) and individual surfactants were used in the experiments; hence, we cannot absolutely exclude a possible influence of solvent diffusion through the water–oil interface on the observed kinetics.

However, we are not inclined to attribute an essential significance to this probable factor, because, in all of the experiments carried out with 12 water- and oil-soluble NSs, in which the content of different solvents amounted to from 50 to 0% depending on the type of a surfactant, the kinetic regularities of an increase in the conductivity of the oil–water system and the pattern of the $G = f(\tau)$ curves remained unchanged, while there were some quantitative differences in the process duration and the $(G - G_0)/G_0$ values.

Let us perform some quantitative estimations for, e.g., a system whose aqueous phase contains Progalit NM 20/40 at a concentration of 10^{-4}% (Fig. 2). The initial equivalent conductivity of this system is 2×10^{-9} S, and its total resistance is, accordingly, 5.0×10^8 Ω. A simple calculation yields the values for the conductivity and resistance of the oil layer equal to $G_2 = 1.67 \times 10^{-8}$ S and $R_2 = 6.0 \times 10^7$ Ω, respectively, and those for the interfacial layer, $G_3 = 2.3 \times 10^{-9}$ S and $R_3 = 4.4 \times 10^8$ Ω. Thus, the resistance of the interfacial layer is 7.3-fold higher than that of the oil layer and its conductivity amounts to 14% of that of the oil layer. At first sight, with regard to the fact that the interfacial layer is much thinner than the oil layer, this finding seems to be strange; however, it may be explained taking into account the asymmetric conductivity of EDL [21]. At certain polarity and voltage applied to EDL, its conductivity may acquire quite low values close to those of dielectrics.

Thus, an analysis of the data obtained leads us to conclude that the revealed kinetics is caused by the combination of several factors, with the contribution of the prevailing adsorption processes that proceed within the time interval under consideration at the water–oil interface.

Figure 4 illustrates the results obtained in preliminary experiments with a water–oil systems containing increased concentrations of mechanical impurities (curve 1) and with an aqueous sodium chloride solution–oil solution of Disolvan-4490 system (curve 2). The qualitative and quantitative features of these curves indicate the possible directions of subsequent studies. The small $(G - G_0)/G_0$ value observed in the former case is, in our opinion, explained by the sedimentation of the mechanical impurities onto the water–oil interface rather than adsorption. In the latter case, the deceleration of the kinetics $G = f(\tau)$ is a reason for investigating the effect of the nature and the concentration of dissolved inorganic salts on the kinetics of EC in oil–water systems.

REFERENCES

1. Waterman, Z.C., *Hydrocarbon Process. Pet. Ref.*, 1965, vol. 44, no. 2, p. 133.
2. Panchenkov, G.M. and Tsabek, L.K., *Zh. Fiz. Khim.*, 1968, vol. 42, no. 5, p. 1244.
3. Panchenkov, G.M. and Tsabek, L.K., *Povedenie emul'sii vo vneshnem elektricheskom pole* (Emulsion Behavior in External Electric Field), Moscow: Khimiya, 1969.
4. Anisimov, B.F. and Emel'yanchenko, V.G., *Kolloidn. Zh.*, 1977, vol. 39, no. 3, p. 528.
5. Lapiga, E.Ya., *Izv. Vyssh. Uchebn. Zaved., Neft Gaz*, 1978, no. 4, p. 95.
6. Vygovskoi, V.P., Mansurov, R.I., and Shutova, Z.M., Available from VINITI, 1981, Ufa, no. 800D.
7. Vygovskoi, V.P., *Cand. Sci. (Tech.) Dissertation*, Moscow: Moskow Inst. of Petrochemical and Gas Industry, 1983.
8. Yunusov, A.A., Babalyan, G.A., and Akhmadiev, G.M., *Khim. Tekhnol. Topl. Masel*, 1987, no. 7, p. 27.
9. Yunusov, A.A. and Babalyan, G.A., *Kolloidn. Zh.*, 1988, vol. 50, no. 2, p. 400.
10. Yunusov, A.A., *Cand. Sci. (Tech.) Dissertation*, Ufa: Ufa Petroleum Inst., 1989.
11. *Emulsion Science*, Sherman, P., Ed., London: Academic, 1968.
12. Mansurov, R.I., Pozdnyshev, G.N., Panchenkov, G.M., and Isanbaeva, A.G., *Tr. Vses. Nauchno-Issled. Inst. Sboru Podgot. Transp. Nefti Nefteprod.*, 1973, no. 11, p. 260.
13. Tronov, V.P., Orlinskaya, V.P., Shireev, A.I., and Isaeva, L.S., *Tr. Tatarsk. Gos. Nauchno-Issled. Proektn. Inst. Neft. Prom-st.*, 1975, no. 33, p. 60.
14. Il'yasova, E.Z., Mansurov, R.I., and Pozdnyshev, G.N., *Tr. Vses. Nauchno-Issled. Inst. Sboru Podgot. Transp. Nefti Nefteprod.*, 1978, no. 21, p. 88.

15. Pozdnyshev, G.N., *Stabilizatsiya i razrushenie nefty-anykh emul'sii* (Stabilization and Breaking of Petroleum Emulsions), Moscow: Nedra, 1982.

16. *Colloid Science,* Kruyt, H.R., Ed., Amsterdam: Elseveir, 1952, vol. 1.

17. Kurlin, M.V., Spirin, A.A., and Frankfurt, Ya.M., *Tr. Leningr. Elektrotekh. Inst.*, 1966, no. 57, p. 48.

18. Bogoroditskii, N.P., Volokobinskii, Yu.M., Vorob'ev, A.A., and Tareev, B.M., *Teoriya dielektrikov* (Theory of Dielectrics), Moscow: Energiya, 1965.

19. Dukhin, S.S., *Elektroprovodnost' i elektrokineticheskie svoistva dispersnykh sistem* (Conductivity and Electrokinetic Properties of Disperse Systems), Kiev: Naukova Dumka, 1975.

20. Lopatin, B.A., *Konduktometriya* (Conductometry), Novosibirsk: Sib. Otd., Akad. Nauk SSSR, 1964.

21. Akhmatov, A.S., *Molekulyarnaya fizika granichnogo treniya* (Molecular Physics of Boundary Friction), Moscow: GIFML, 1963.