INFLUENCE OF THE COMPOSITION AND TEMPERATURE OF CONCENTRATED MAGNETIC FLUIDS ON THEIR ELECTROPHYSICAL PROPERTIES FOR DIFFERENT FREQUENCIES OF THE ELECTRIC FIELD

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A study has been made of the regularities determining the electrophysical properties of magnetic fluids based on decane, turbine oil, water, and kerosene as functions of the frequency of the electric field, the concentration of the dispersed phase, and the temperature. The optimum frequencies of the electric field, concentration of the dispersed phase, and temperatures within which the electrophysical characteristics, such as the relative permittivity, the specific electrical resistance, and the dielectric loss tangent, turn out to be the most informative for evaluation of the structure, compositions, and properties of magnetic fluids have been determined.

Introduction. Physicochemical processes occurring in magnetic fluids (MFs) are accompanied by electric phenomena of different kinds, which can be of importance in formation of a structural state in them. Magnetic fluids as colloidal disperse systems possess a pronounced structural dynamics whose change is accompanied by the transfer and redistribution of free and coupled charges between the dispersed phase and the dispersion medium and has an effect on the character of conduction. From this viewpoint, it seems expedient to employ the dielectric-spectroscopy method for monitoring of the compositions and properties of magnetic liquids by their electrophysical characteristics, such as the relative permittivity ε, the specific electrical resistance ρ, and the dielectric loss tangent $\tan \delta$.

Procedure. For experimental investigations we have developed a procedure ([1]) the basis for which is separate measurement of the capacitive and active components of the impedance of an electrode cell with an MF in the range of electric-field frequencies 10^2–10^7 Hz and the interval of temperatures 247–353 K. The MF specimens under study were placed in a uniform electric field produced in the interelectrode space of a measuring cell with plane-parallel electrodes. The influence of "spurious" parameters on the results of measurements of the capacitance and conductance of the electrode cell with an MF was eliminated by correction of the components of impedance. The relative permittivity, the specific electrical resistance, and the dielectric loss tangent of the MFs were calculated from the corrected values of the capacitance and conductance of the electrode cell with an MF. The electric parameters of the MF specimens were measured in thermostatting of the electrode cell. The measurement accuracy for the capacitance and conductance of the electrode cell with an MF amounted to $\pm 0.5\%$.

Experimental Results. We have studied the regularities determining the electrophysical properties of MFs as functions of a frequency of the electric field of 10^2 to 10^7 Hz, the concentration of the dispersed phase (to 35%), and a temperature of 247 to 353 K. We employed MFs based on decane [2], turbine oil [3], water [4], and kerosene [5] with oleinic acid as a surfactant.

What the MFs based on turbine oil, decane, and water have in common is that the absolute values of ε, ρ, and $\tan \delta$ in them decrease with increase in the electric-field frequency (Figs. 1 and 2). At the same time, we observe a significant difference in the profiles of frequency dependences of the above electrophysical characteristics, as the degree of polarity of the dispersion medium (oil–water or decane–water) changes. Whereas the change in the quantities ε and ρ for the MF based on turbine oil or decane is characterized by an abrupt decay on a fairly limited portion of frequencies, the quantity ρ for the water-based MF depends on the frequency only slightly, which is due to the influence of the permittivity of the dispersion medium. For the water-based MF we observe a characteristic decrease in the
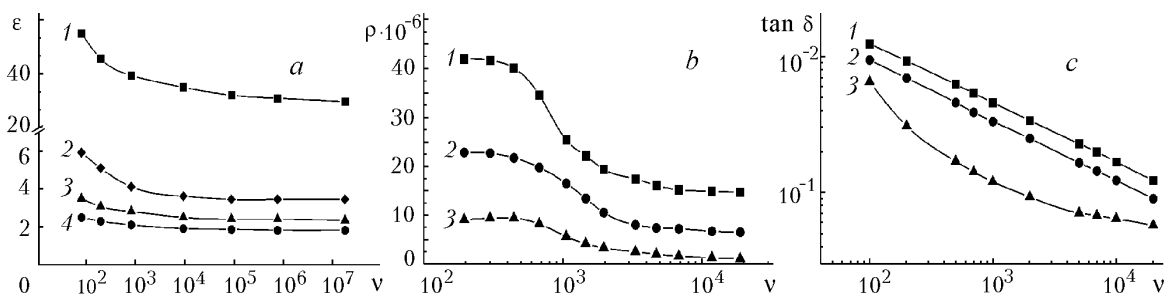
Fig. 1. Frequency dependence of the relative permittivity (a), specific electrical resistance (b), and dielectric loss tangent (c) of a turbine-oil based MF (T = 293 K): a) C = 30; 2) 11; 3) 6.5%; 4) turbine oil; b and c) 1) C = 6.5; 2)
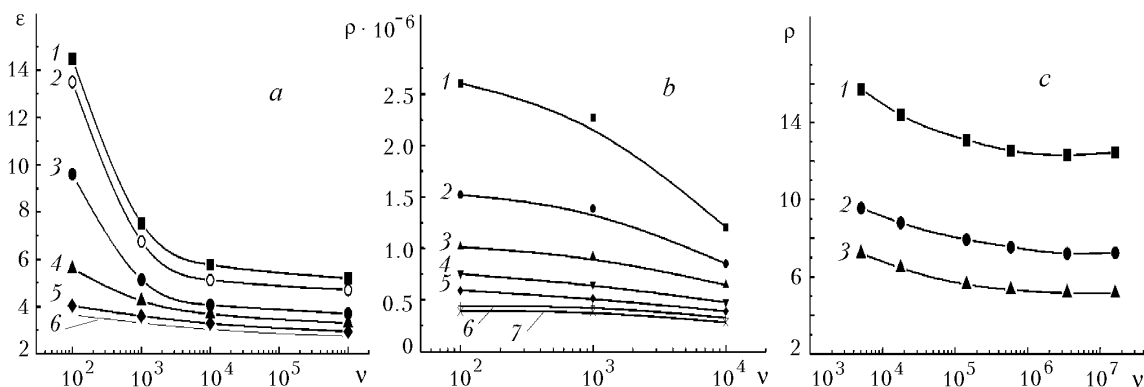

Fig. 2. Frequency dependence of the relative permittivity of a decane-based MF (a) and the specific electrical resistance of decane-based (b) and water-based MFs (c) (T = 293 K): a) 1) C = 35; 2) 30; 3) 25; 4) 20; 5) 15; 6) 5%; b) 1) C = 5; 2) 10; 3) 15; 4) 20; 5) 25; 6) 30; 7) 35%; c) 1) C = 6.5; 2) 11; 3) 30%.

quantities ρ with increase in the concentration of the dispersed phase and accordingly a decrease in the concentration of water as the electrolyte, which, in our opinion, is attributed to the influence of supermicellar structural formations generated in concentrated MFs depending on the concentration of the dispersed phase (see Fig. 1a and b and Fig. 2). At the same time, the absolute values of ε, ρ, and tan δ of the MFs are substantially changed (by 1 to 5 orders of magnitude).

The observed frequency dependences of ε, ρ, and tan δ of the MFs are attributed to the character of the traversal of the electrode cell with an MF by an electric current of different frequency and are associated with the accumulation of space charge at the phase boundary (electrode–MF, dispersion medium–protective surfactant layer, protective surfactant layer–dispersed-phase particle). An additional contribution to the process of polymerization due to the relaxation of dipole molecules is made for the MF produced on the basis of a polar liquid. At low frequencies, when the relaxation time is too short as compared to the period of electric oscillations, the charge has time to accumulate at the phase boundary and the quantity ε attains relatively high values. Under these conditions, the monomolecular protective surfactant layer covering the polydisperse particles of magnetite possesses a fairly high electrical resistance. As the frequency increases, the relaxation time turns out to be longer than the period of electric oscillations and the electrical resistance of the protective surfactant layer decreases, which provides real conditions for traversal of the magnetite particles by the alternating current. This leads to an increase in the cross section of the conducting component and accordingly a decrease in the value of ρ of the MF.

The results of investigations of the electrophysical characteristics of MFs based on decane (Fig. 3), kerosene (Fig. 4), turbine oil, and water (Fig. 5) as functions of the concentration of the dispersed phase demonstrate that the increase in the content of the dispersed phase in an MF leads to an increase in ε and a decrease in ρ of the MF (see Fig. 3a, Fig. 4, and Fig. 5). The dependence of the dielectric loss tangent of the decane-based MF on the concentra-
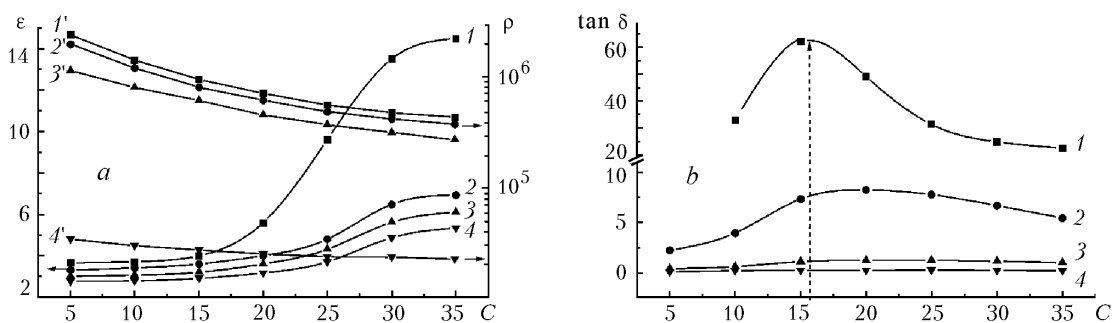
Fig. 3. Concentration dependences of the permittivity, the specific electrical resistance (a), and the dielectric loss tangent (b) of a decane-based MF (T = 293 K): a) 1 and 1′) ν = 10^2; 2 and 2′) 10^3; 3 and 3′) 10^4; 4 and 4′) 10^6 Hz; b)
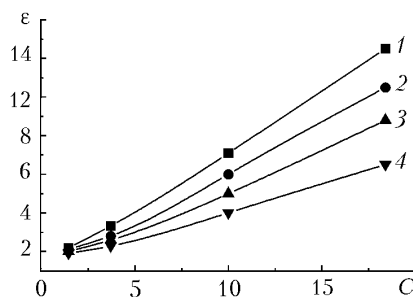

Fig. 4. Concentration dependence of the permittivity of a kerosene-based MF (T = 293 K): 1) ν = 10^2; 2) 10^3; 3) 10^4; 4) 10^6 Hz.

tion of the dispersed phase is nonlinear in character and has a maximum (see Fig. 3b). The quantities ε and ρ of the decane-based MF in the region of high concentrations of the dispersed phase ($C > 30\%$) approach constant values, while the maximum of the quantity tan δ is found in the region of critical concentrations.

The results of an analysis of the concentration dependences of ε, ρ, and tan δ of the studied MFs based on decane, kerosene, turbine oil, and water demonstrate the existence of the critical region of the dispersed phase (10–20%), which is characterized by a pronounced change in the character of conduction of the MFs (see Fig. 3, Fig. 4, and Fig. 5). As follows from the data obtained, when the concentrations are relatively low, we have the most pronounced change in ρ since the main contribution to the conductance is made by free charges. The quantity ε, conversely, changes more in the region of high concentrations, which is attributed to the predominance of polarization phenomenon. The dielectric loss tangent experiences a pronounced change whose extremum value lies in the region of critical concentrations of the dispersed phase (see Fig. 3b). This allows the assumption on qualitatively different structural states of the MFs with relatively low and high concentrations of the dispersed phase.

The increase in the electric-field frequently leads to a decrease in the quantities ε and ρ of the decane-based MF. The maximum of the quantity tan δ of the MF shifts toward higher concentrations and has a smoother form. The quantity ε of the MF specimens under study depends on the concentrations of the dispersed phase at all the frequencies under study (10^2, 10^3, 10^4, and 10^6 Hz). The most significant changes in ε (of approximately 5 times) in the case where the concentration of the dispersed phase in the decane-based MF increases to 35% are observed at a frequency of 10^2 Hz. In the investigated range of concentrations of the dispersed phase, the quantity ρ, unlike ε, is the most informative just at frequencies of 10^2, 10^3, and 10^4, whereas the quantity tan δ is informative at 10^2 and 10^3 Hz. The quantity tan δ of the MF at a frequency of 10^6 Hz has a smoother form and is independent, in practice, of the concentration of the dispersed phase (see Fig. 3).

The results of investigations of kerosene-based MFs demonstrate that the quantity ε exhibits a virtually linear dependence on the concentration of the dispersed phase at all the frequencies under study (10^2, 10^3, 10^4, and 10^6 Hz). The most significant changes in the quantity ε (of approximately 7 times) with increase in the concentration of the dispersed phase (to 18%) have been established at a frequency of 10^2 Hz (see Fig. 4). Consequently, the dielectric-spec-
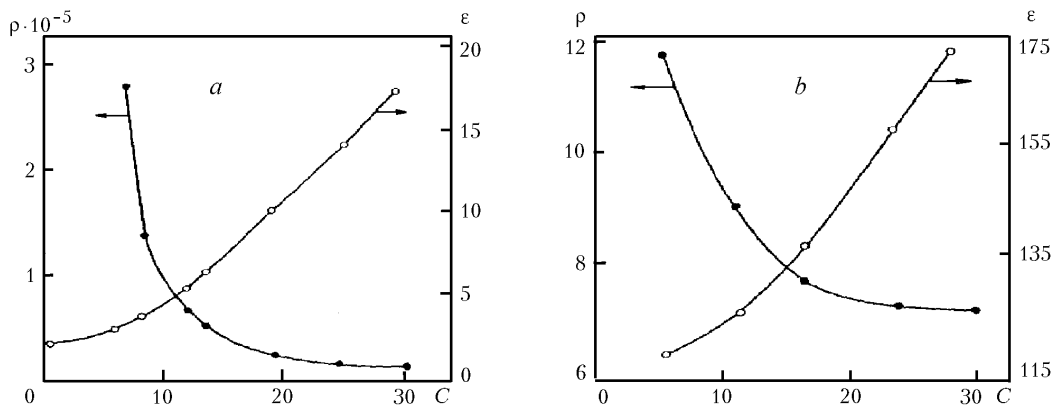
Fig. 5. Concentration dependences of the permittivity and the specific electrical resistance of turbine-oil-based (a) and water-based (b) MFs respectively: $\nu = 5 \cdot 10^6$ Hz and $T = 293$ K.
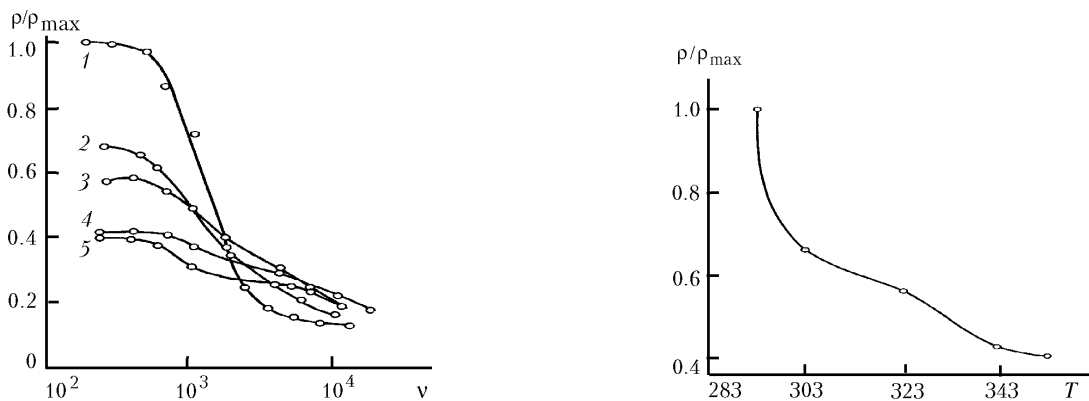

Fig. 6. Frequency dependence of the ρ/ρ_{max} ratio of a turbine-oil-based MF for different temperatures: 1) 293; 2) 303; 3) 323; 4) 343; 5) 353 K; $C = 30\%$.

Fig. 7. Temperature dependence of ρ/ρ_{max} ratio of a turbine-oil-based MF: $\nu = 5 \cdot 10^2$ Hz and $C = 30\%$.

troscopy method can successfully be employed for both monitoring of the concentration of the dispersed phase and control of the technology of production of an MF by the data of its permittivity based on the constructed and statistically substantiated standard curves.

The analysis of the results of investigations of ε, ρ, and tan δ of MFs as functions of their composition has enabled us to determine the optimum region of operating frequencies within which the electrophysical characteristics turn out to be the most sensitive to a change in the concentration of the dispersed phase in the MFs. When the composition of an MF is fixed (which, in actual practice, means the use of the same method of synthesis), the electrophysical characteristics can be employed as the criterion characterizing the concentration of the dispersed-phase particles in the MF. The corresponding evaluation of this parameter in the MF is carried out by the electrophysical quantity determined at a frequency of 10^2 Hz as the most sensitive to a concentration change of the dispersed-phase particles. We emphasize that in the region of concentrations of the dispersed phase of 5–20%, the most sensitive electrophysical characteristics are the specific electrical resistance and the dielectric loss tangent of an MF, whereas in the region of concentrations of the dispersed phase of 20–35% preference should be given to its permittivity.

The increase in the temperature from 293 to 353 K leads to a significant decrease in the quantity ρ of the turbine-oil-based MF. Noteworthy is the character of the temperature dependences in the region of frequencies $1 \cdot 10^3$–$8.5 \cdot 10^3$ Hz inherent in turbine-oil-based MFs with a concentration of the dispersed phase of 30% (Fig. 6). When the temperature increases even from 293 to 303 K, we find two smooth transitions, approximately at a frequency of
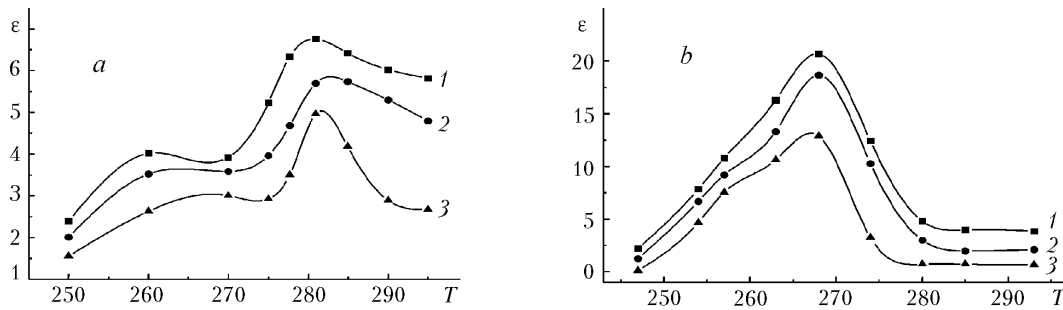
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Fig. 8. Temperature dependence of the permittivity of a kerosene-based MF for different frequencies of the electric current: a and b) C = 3.6 and 18.4 wt.% respectively: 1) $\nu = 10^2$; 2) 10^3; 3) 10^4 Hz.

$1 \cdot 10^3$ and $8.5 \cdot 10^3$ Hz, on the profile of the dispersion curve. Apart from these features, the temperature dependences enable us to single out the existence of thermolabile states in MFs with a relatively high content of the dispersed phase (Fig. 7).

The temperature dependences of the permittivity for the kerosene-based MF in the interval 247–293 K significantly differ from the MFs described earlier (Fig. 8).

We have found experimentally for the first time a shift of the hardening temperature (T_{max}) of colloids and of the permittivity extrema $\varepsilon(T_{max})$ toward lower temperatures with increase in the concentration of the dispersed phase in a kerosene-based MF [5]. The changes in the quantity ε in the vicinity of the characteristic temperatures of hardening of colloids in the phase transition found in the kerosene-based MF are insignificant. The maximum recorded shift of the hardening temperature of colloids in the kerosene-based MF is approximately 8.5 K, as the calculation of the dispersed phase increases from 3.6 to 18.4% (see Fig. 8). The effect found is explained by the fact that the processes of solvation are of considerable importance in this phenomenon and that the maximum $\varepsilon(T_{max})$ revealed is specific to liquid magnetics, since the temperature dependences of the viscosity and the permittivity of MFs are interrelated to the processes of relaxation of the magnetic moment of magnetite particles.

The results obtained demonstrate that a real magnetic fluid represents a multicomponent system which consists of small aggregation-stable superparamagnetic particles, solid nondestructible clusters, and individual large particles capable of quasi-back-aggregation with decrease in the temperature. The fractions of large particles about several hundreds angströms in size are close in properties to a real van der Waals gas. At elevated temperatures, the particles are in the superparamagnetic phase, but when the temperature decreases the particles, condensing, change to a cluster form [6].

It is of particular interest to note the fact that in investigating the temperature dependences of the acoustic properties of transformer-oil-based MFs, a concentration change of the magnetic phase from 0 to 28% does not cause the maximum of the ultrasound-damping coefficient to shift by within 1 K. But in water-based MFs, a concentration change of the magnetic phase from 0 to 8% causes the crystallization temperature (and consequently the maximum of the velocity of ultrasound and the damping coefficient) to shift by approximately 4 to 5 K [7].

Conclusions. The electrophysical characteristics of MFs turn out to be very sensitive to a change in the concentration of the dispersed phase and the temperature of the medium. The analysis of the regularities determining the change in the electrophysical characteristics of an MF as a function of the frequency of the electric field, the concentration of the dispersed phase, and the temperature of the medium has enabled us to reveal the tendencies toward improving the efficiency of electric-charge transfer and to determine requirements for experimental conditions and the parameters of MFs which contribute to the optimum manifestation of the phenomena in question.

NOTATION

C, concentration of the dispersed phase, %; T, temperature, K; ε, relative permittivity; ν, frequency at which the measurement is carried out, Hz; ρ, specific electrical resistance, $\Omega \cdot m$; $\tan \delta$, dielectric loss tangent. Subscript: max, maximum.

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