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Effect of a near-surface nanolayer formation on the magnetic fluid electrical properties[1]

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Abstract. In a magnetic colloid- a magnetic fluid (MF), which is placed in an electrochemical cell (a flat capacitor), a thin near-surface layer is formed in the electric field. This layer is an active medium in which the process of self-organization – autowaves was observed and studied. The layer consists of magnetite particles with a protective coating—oleic acid (HOl). We found a several orders increase of capacitance and a few times increase in the resistance of an electrochemical cell filled with a magnetic fluid by sending a pulsed electric field to the electrodes. Electrodes in the cell are thin transparent conductive ITO ($InSnO_2$) membranes deposited on the glass. The cell reflectivity (reflectance) changes due to the formation of the near-electrode layers of magnetic fluid nanoparticles in the electric field. It can be registered by the interference of the falling light in these layers. The thickness of the near-electrode layer is estimated from the change in the reflectivity of monochromatic light. With increasing voltage on the electrodes, the layer becomes unstable, it periodically arises and collapses. As a result, the intensity of the reflected light fluctuates. When illuminated with white light, brightly colored waves are visible on the surface of the cell.

Key words. Polarization capacitance, magnetic fluid, near-electrode nano-layer, autowaves.

1. Introduction

Magnetic fluid (MF) is a stable colloid of single-domain ferromagnetic particles (magnetite) dispersed in various liquids (kerosene, water, etc.) [1]. The effect of an electric field on the magnetic fluids leads to a number of interesting phenomena: a change in the reflectivity of a cell with MF, formation of a layer of close-packed

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magnetite particles with a protective coating near the electrode, and the appearance of autowaves [2]. In the absence of an electric field, the magnetic fluid, placed in a cell between two electrodes is homogeneous [3]. When the field is turned on, the particles of the solid phase start migrating under the influence of electrophoresis and dipolophoresis, and on the surface of the electrodes the concentration of magnetite particles increases to a value of 25–27 % vol., so the near-electrode layer is formed. This layer is a unique active medium in which an autowave process is observed. The purpose of this paper is to show that the formation of a near-electrode layer consisting of magnetite nanoparticles affects the increase in the capacitance and conductivity of an electrochemical cell with a magnetic fluid.

2. Materials and methods of the experiment

A magnetic fluid of the "magnetite in kerosene" type was used in the experiment. The concentration of magnetite is 3.2 % vol. Dielectric permittivity of fluid $\varepsilon = 2.1$, conductivity $\sigma = 3.8 \cdot 10^{-7}\,\Omega\mathrm{m}^{-1}$ (measured at a frequency of 1000 Hz). The average size of magnetite particle is $\sim$ 10 nm. The experimental device is shown in Fig. 1. The magnetic fluid was placed in an electrochemical cell, consisting of two electrodes made of glass with a conductive transparent coating $\mathrm{InSnO_2}$ (ITO). The electrode surface area $S = 40 \times 30\,\mathrm{mm}^2$. The glass thickness of the samples is 4 mm, the thickness of a conductive coating is $h_0 = 160 \pm 5\,\mathrm{nm}$, the thickness of the magnetic fluid layer $l = 40\,\mu\mathrm{m}$ (Fig. 1A). The capacitance of the electrochemical cell (static capacitance), calculated by geometric dimensions, measured at a frequency of 1000 Hz is $C_{\mathrm{st}} = 6 \cdot 10^{-10}$ F.

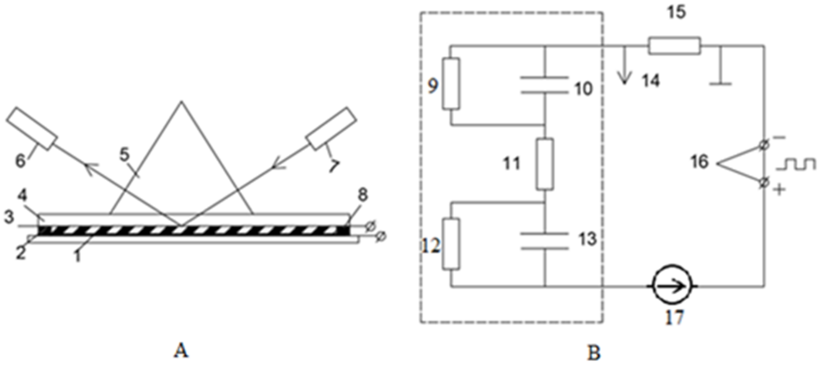
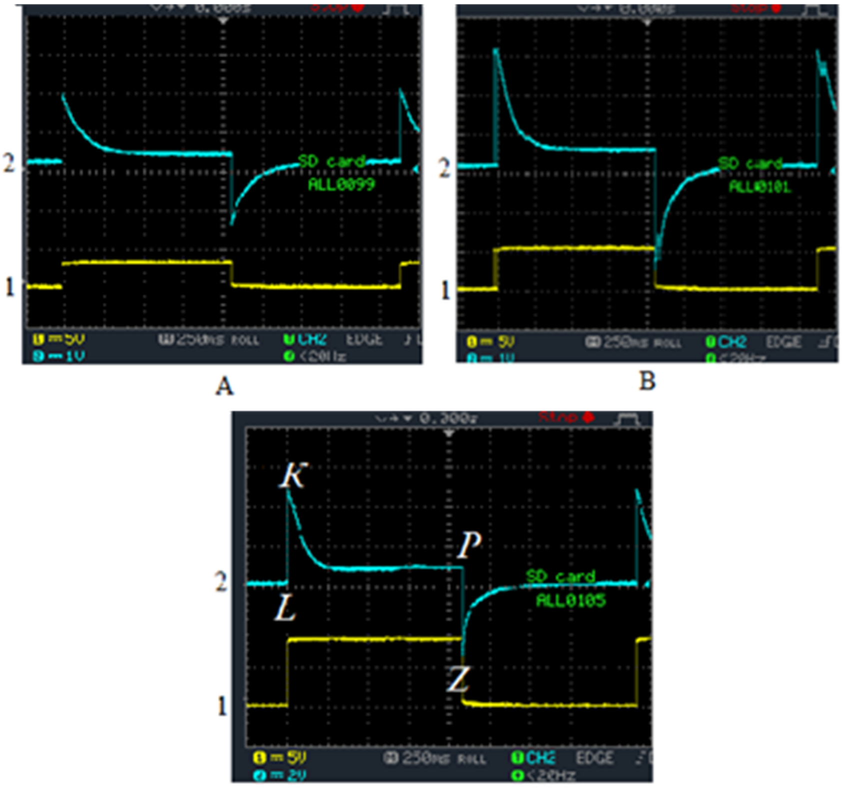


Fig. 1. Scheme of the experimental device. A–cell with a MF; 1–magnetic fluid, 2 and 4–transparent conductive coated glass (ITO), 3 and 8–insulating gaskets, 5–prism, 6–photodiode, 7–illuminator (laser), B–equivalent circuit of electrical measurements (the equivalent circuit of the cell with the MF is dashed); 9 and 12–R_1, R_3 (resistances of near-electrode layers), 10 and 13–C_2, C_5 (capacitances of electrode layers), 11–R_2 (resistance of interelectrode layer), 14–oscilloscope input, 15–R_4 (oscilloscope shunt), 16–terminals connected to the output generator of unipolar rectangular pulses, 17–EMF of electro-chemical (Faraday) polarization

The electrodes 16 (Fig. 1B) were supplied with rectangular pulses: amplitude U, impulse length is half of a period. The pulse period was 2.2 s. Front is less than 1 µs. The output resistance of the generator is 600 Ω.

When switching on the pulse voltage, the current through the shunt ($10^5\,\Omega$) passes through the cell with the MF. The dependence of the current on time was recorded with the oscilloscope (Figs. 2 A,B,C)



A

B

C

Fig. 2. Beams #1–dependence of the current flowing through cell on time, beams #2–impulse voltage U at the electrode: A–$U = 2.5\,\mathrm{V}$, B–$U = 4\,\mathrm{V}$, C–$U = 6\,\mathrm{V}$

At the moment of the electric pulses switching on and off, the current is maximal (points K and Z in Fig. 2C), after a time $\tau \sim 200\,\mathrm{ms}$ the current becomes stationary. After applying a voltage in the cell, a layer of particles forms near each electrode, and we assume that this is the cause of the change in the current value.

We show below how we detected the formation of a near-electrode layer using the method of electrically controlled interference [4, 5]. Electrically controlled interference (electrointerference) occurs when light is reflected from electrodes in an electrochemical cell with a magnetic fluid. In an electric field, the particles of the dispersed phase (magnetite) migrate to the electrodes. In this case, the optical properties of the medium near the transparent electrode change (the complex refractive index increases). The reflected light properties change as well. When the cell surface is illuminated with monochromatic light, the reflectivity of the reflected ray varies periodically with the layer growth. By registering the change in the intensity of the reflected beam (optical response), we can state that the near-electrode layer was formed and we can measure its thickness by the method described in [4]. The method for obtaining the optical response is as follows (Fig. 3): the laser beam (1 mm in diameter, wavelength $\lambda = 650\,\text{nm}$, TE-polarization) was directed to the surface of the MF cell. The beam was reflected from the "glass–ITO membrane", "ITO membrane is a layer of magnetite particles" and "layer of magnetite particles–MF" surfaces and entered the photodiode. It is connected to the input of a double-beam oscilloscope GDS-71022, which allows recording the voltage change on a photodiode FD-256 (optical response) with time (Fig. 4, beam 1 and Fig. 3).

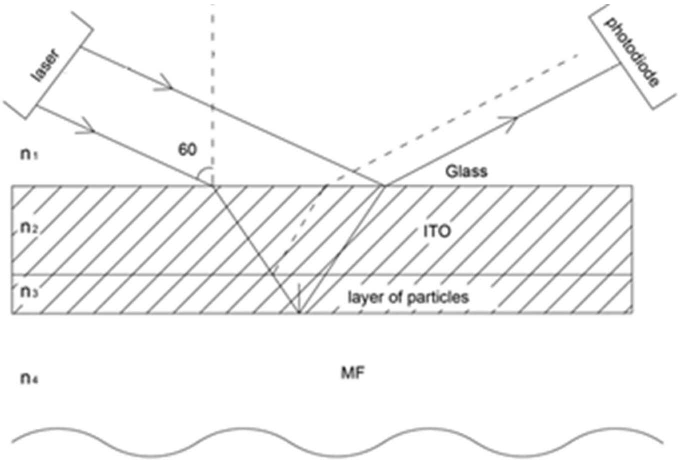


Fig. 3. Model of multilayer structure "glass-ITO—layer of particles—MF" with the course of the rays

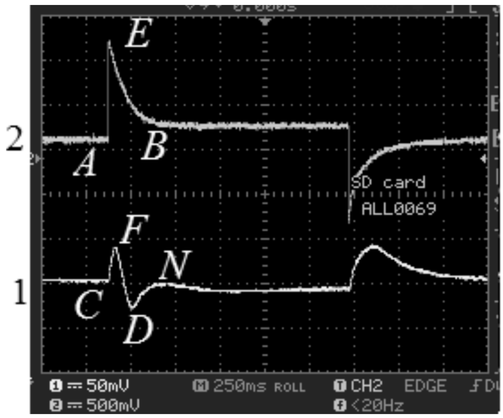


Fig. 4. Beam 1—optical response of the reflected beam (voltage on photodiode), beam 2–dependence of cell current with the magnetic fluid on time

We note that the change in the near-electrode layer thickness is fixed precisely by the optical signal [5]. Beam 2 on the oscillogram in Fig. 4 is the dependence of the current in the cell with the magnetic fluid on time. The section AEB corresponds to a change in the current in the cell when the electric pulse is turned on.

Comparing the sections AEB (beam 2) and CFDN (beam 1), we can see that a change in the current through the cell occurs simultaneously with the formation of a near-electrode layer of magnetite nanoparticles. These observations give us reason to conclude that the reason for the change in cell current is the formation of near-electrode layers.

3. Results

3.1. Resistance calculation of the electrode layers

The oscilloscope GDS-71022 used in the experiments allows not only to derive the current dependence through the cell $i(t)$ on the screen (Figs. 2 and 4), but to write to the Ecxel file: 1000 data units for one second (Fig. 5). For calculations it is convenient to use the graph obtained from these data.

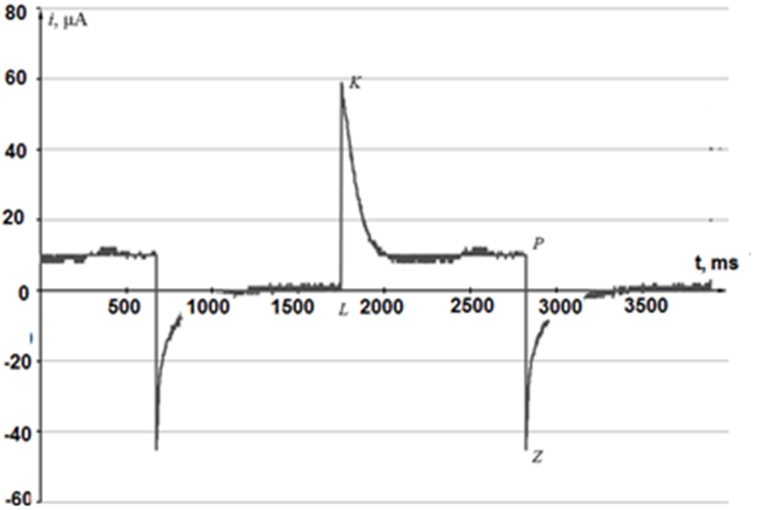


Fig. 5. Dependence of current in a cell with a magnetic fluid on time, impulse voltage on the electrodes $U = 8\,\mathrm{V}$

By the maximum value of the current $i_{\max} = 58\,\mu\mathrm{A}$ at the moment of switching on (point K in Fig. 5) and the voltage in the pulse $U = 8\,\mathrm{V}$, we found the cell resistance before the appearance of the near-electrode layer–$R_{\text{before}} = 1.4 \cdot 10^5\,\Omega$. As expected, it is equal to the resistance of the cell, measured for alternating current. The stated current is $\approx 10\,\mu\mathrm{A}$. So the cell resistance, after the formation of layers, is $R_{after} = 8 \cdot 10^5\,\Omega$. Thus, after the formation of the layers, the resistance of the cell with the magnetic fluid increased six times. In the experiment, the currents in the cell i_1 (voltage on) and i_2 (voltage off) are equal to each other within the error of the experiment (sections KL and PZ in Figs. 2C and 5) and are determined by the formulas

$$i_1 = \frac{U - E}{R_\mathrm{c}}, \tag{1}$$

$$i_2 = \frac{U + E}{R_\mathrm{c}}, \tag{2}$$

where R_c is the resistance of a cell with a magnetic fluid, E is the EMF of electrochemical (Faraday) polarization (Fig. 1B). The signs "+" and "-" in EMF in formulas (1) and (2) are related to the fact that the charge current i_1 and the discharge current i_2 have different directions. Consequently, the EMF of the electrochemical (Faraday) polarization is much less than the voltage in the pulse and can be ignored. By the difference in resistance before and after the formation of layers, the sum of the near-electrode layers resistances was found: $R_\mathrm{ls} = (6.6 \pm 0.5) \cdot 10^5\,\Omega$.

3.2. Resistance calculation of the electrode layers

The charge Q, accumulated in the cell, can be found by integrating the dependence of $i(t)$ on time from the moment of switching off the voltage (point Z in Fig. 5) to $i = 0$.

$$Q = \int_{t_1}^{t_2} i \,\mathrm{d}t = (6.9 \pm 0.3) \cdot 10^{-6}\,\mathrm{C}, \tag{3}$$

where $t_1 = 0$ is the moment of switching off the voltage and $t_2 = 1.1\,\mathrm{s}$.

It is known that the capacitance associated with the dependence of its magnitude on the voltage and time of electric current flow (polarization capacitance) can be calculated by the formula

$$C_\mathrm{pol} = Q/U\,. \tag{4}$$

For the voltage $U = 7\,\mathrm{V}$ on the electrodes, it is $(0.9{\pm}0.1){\cdot}10^{-6}\,\mathrm{F}$, for the voltage $U = 5\,\mathrm{V}$ the capacitance is $(1.3{\pm}0.1){\cdot}10^{-6}\,\mathrm{F}$, and for the voltage $U = 5\,\mathrm{V}$ the capacitance is $(2.2{\pm}0.3){\cdot}10^{-6}\,\mathrm{F}$.

3.3. Change in the cell capacitance and the resistance of the near-electrode layers is the cause of the self-oscillations of the near-surface layer

The thickness of the near-electrode layer was calculated by the oscillogram in Fig. 5 and equals $\sim$ 100 nm. At a voltage $U = 15\,\mathrm{V}$, local self-oscillations arise which were fixed by the oscillations of the optical signal (Fig. 6A). The oscillogram in Fig. 6A was obtained when the voltage divider 1:10 that was switched on to the oscilloscope input (channel 2).

After the transient process, the oscillations become regular and an autowave process starts in the cell (Fig. 6B).

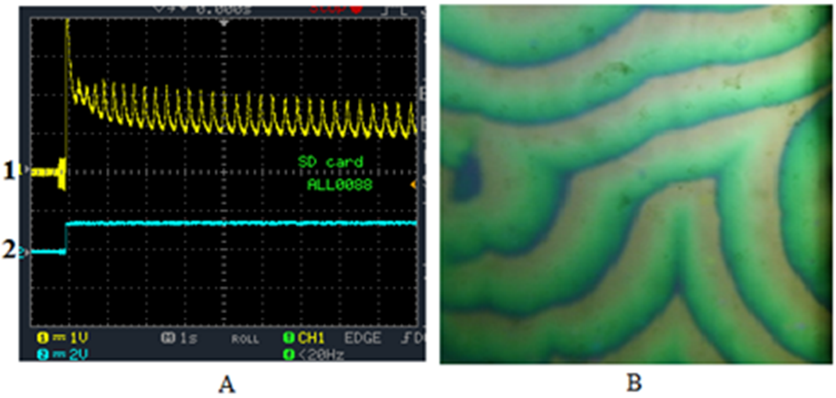


Fig. 6. Autowave process in the electrochemical cell with a MF; A-–oscillogram of the process (beam 1–optical signal oscillations during autowaves appearance, beam 2–impulse voltage); B–photograph of the steady-state autowave process in the electrochemical cell with the MF (40 seconds after the electric field switching on); frame width is 1.2 cm

4. Conclusion

The properties of the electrochemical cell with transparent electrodes filled with a weakly conducting dielectric—a magnetic fluid was researched. Rectangular electric pulses were applied to the electrodes, and a polarization capacitance was calculated from the measured current in a cell with a magnetic fluid. It is established that the polarization capacity of the cell is greater than the static capacity by 3–4 orders of magnitude. This phenomenon is attributed to the formation of thin (~ 100 nm) near-electrode layers consisting of a magnetic fluid dispersed phase particles (magnetite) with a protective shell. The resistance of a cell with a magnetic fluid is calculated after the formation of near-electrode nanolayers, which is several times higher than the cell resistance before the electric impulses are applied to the electrodes. It is shown that when the voltage higher than 11 V is applied to the electrodes, the field strength in the near-electrode layer reaches a value of more than $2.3 \cdot 10^7$ V/m, at which the layer resistance drops sharply, it becomes conductive (Wine effect). The particles from which the layer consists, repel and come into the liquid, where they are discharged and the process repeats. Local self-oscillations arise, and brightly colored autowaves can be observed near the surface of the electrode.

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