
LIQUID
CRYSTALS

Impedance Spectroscopy Investigation of Liquid Crystals Doped with Ionic Surfactants

B. A. Belyaev^{a, b, c, *}, N. A. Drokin^a, and A. N. Maslennikov^a

^a *Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia*

* e-mail: belyaev@iph.krasn.ru

^b *Siberian Federal University, pr. Svobodnyi 79, Krasnoyarsk, 660041 Russia*

^c *Reshetnev Siberian State Aerospace University,
pr. Imeni Gazety "Krasnoyarskii Rabochii" 31, Krasnoyarsk, 660014 Russia*

Received January 16, 2014

Abstract—The effect of a direct-current (dc) electric field on the electrophysical characteristics of nematic liquid crystals of the alkyl cyanobiphenyl series nCB ($n = 6–8$) and the multicomponent liquid-crystal mixture MB-1, which are doped with ionic surfactants, has been investigated using impedance spectroscopy. It has been found that the impedance spectra depend substantially on the dc bias voltage applied to the sample. The approximation of the measured spectra with specially developed equivalent circuits of the measuring cell with a sample has made it possible to determine the capacitance of the electric double layer and the electrical conductivity of the samples, as well as the mobility, concentration, and diffusion coefficient of the ions. It has been shown that a region of the space charge is formed in the frequency range $f < 100$ Hz near the electrodes of the measuring cell with a liquid-crystal sample, which leads to an increase in the active (resistive) and reactive (capacitive) components of the impedance.

DOI: 10.1134/S106378341407004X

1. INTRODUCTION

As is known, liquid crystals are dielectrics. However, even liquid-crystal samples that are well purified from ionic impurities can have a significant conductivity due to the adsorbed moisture and the formation of ions during the dissociation of molecules, but a particularly strong increase in the conductivity occurs when the mesophases are doped with ionic surfactants. Surfactants, as a rule, have been used to modify metal surfaces of a liquid-crystal cell with the aim of creating the initial normal or homeotropic orientation of the director. The occurrence of ionic conduction is usually considered as an undesirable phenomenon, because the flow of electric current through the liquid-crystal cell is accompanied by different effects of electric charge accumulation and relaxation near the electrodes, which deteriorate the quality of liquid-crystal displays and various devices used in electronics and microwave technology. However, under specific conditions, changes in properties of the mesophase due to the presence of ions in the liquid crystal can be very useful. For example, it was shown in [1] that the measuring cell with an ion-containing liquid-crystal compound can act as a generator of low-frequency oscillations induced as a result of the formation of an auto-soliton at the cathode, its motion, and disappearance at the anode. In [2], the authors proposed a new design for multichannel modal correctors that made it possi-

ble to control the form of the wave front of electromagnetic radiation passing through the liquid-crystal cell.

Of particular interest for the use in practice are various orientational structural transitions of the mesophase (local Frederiks transitions) due to the change in the surface adhesion of liquid-crystal molecules with the electrode of the measuring cell [3]. The degree of adhesion of liquid-crystal molecules with the surface of the cell can be changed in different ways. In [4], it was shown, in particular, that the effective re-orientation of molecules of the liquid-crystal phase can be achieved under the influence of an electric field acting on the ferroelectric polymer coating of the electrodes. Interesting possibilities for controlling the orientation of the liquid crystal are provided by the effects photoinduced in a photoorientant layer deposited on the electrode surface [5]. In [6], the change in orientation properties of the surface was achieved by the injection of charges in the polymer–liquid crystal structure.

There are also possibilities for reorienting the director in cells with a liquid crystal doped with ionic surfactants. In this case, after the dissociation, the surfactant molecules are partially adsorbed on the electrode surfaces and simultaneously exist in the form of oppositely charged ions in the bulk of the liquid crystal. In an electric field, the displacement of ions toward the corresponding electrodes can change the

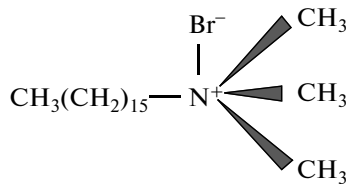


Fig. 1. Chemical formula and molecular structure of the CTAB ionic surfactant.

concentration of adsorbed surfactant molecules, which leads to a modification of the surface orientation of the director. This method of controlling the molecular structure of the liquid crystal was tested in [7] on droplet ensembles of the 5CB nematic liquid crystals, which have a positive dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} > 0$, and methoxybenzylidene butylaniline (MBBA) with a negative anisotropy $\Delta\epsilon < 0$. Here, ϵ_{\parallel} and ϵ_{\perp} are the parallel and perpendicular components of the relative permittivity, respectively. In order to implement and develop the ionic methods for controlling the orientation of liquid-crystal molecules, it is important to know the dependences of the ionic conduction of the liquid-crystal sample in the measuring cell, as well as the processes of charge accumulation and transfer near the metal electrodes, on the frequency and strength of the control electric field.

In this work, the electrophysical characteristics of liquid crystals of the alkyl cyanobiphenyl series and the liquid-crystal mixture MB-1, doped with ionic surfactants and placed in a special cell, have been investigated experimentally. The investigation has been performed by the method of measuring the complex impedance of the cell under the influence of direct-current (dc) and alternating-current (ac) electric bias fields acting on the liquid crystal in the frequency range from 0.1 Hz to 100 MHz.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

The experiment was performed using a standard cell consisting of two plane-parallel glass substrates with electrodes located on their inner sides and prepared from indium oxide with tin, which had a surface area $S \sim 10 \times 10$ mm and a gap $d \sim 0.05$ – 0.10 mm. These electrodes have been widely used in electro-optical devices, because they are optically transparent and chemically stable and have a relatively low surface resistance of $\sim 20 \Omega/\square$. The control measurements were performed using electrodes with aluminum and gold films evaporated on glass substrates. The electrode surfaces were not specially treated, but they were only slightly rubbed with a soft skin. This promoted spontaneous orientation of the long axes of the liquid-crystal molecules at a small angle ($\sim 5^{\circ}$ – 7°) with respect to the surface of the electrodes.

The objects of investigation were liquid crystals of the alkyl cyanobiphenyl series 6CB, 7CB, and 8CB, as well as the multicomponent liquid-crystal mixture MB-1 with the temperature of the transition from the nematic to isotropic state $T \geq 100^{\circ}\text{C}$. The samples 6CB and 7CB contained some concentration of ions introduced with random impurities. Therefore, they had not only the ac conductivity but also the dc conductivity. In the liquid crystals 8CB and MB-1, the intrinsic dc conductivity was not observed. However, in these liquid crystals, as should be expected, the doping with an ionic surfactant, namely, cetyltrimethylammonium bromide (CTAB), led to the appearance of dc conductivity, which at a CTAB concentration of ~ 1 wt % and temperature $T = 70^{\circ}\text{C}$ was comparable to the conductivity of the samples 6CB and 7CB. The chemical formula and molecular structure of the CTAB ionic surfactant are shown in Fig. 1.

The CTAB molecule is a polar molecule with a dipole moment concentrated in the group $-\text{N}-(\text{CH}_3)_3$. The length of the molecule amounts to 2.33 nm, which is comparable with the length of the liquid-crystal molecules, and the diameter of the “head” is approximately 0.48 nm [8]. In liquid crystals, the CTAB molecules dissociate into a negatively charged bromine ion Br^- and a positively charged backbone CTA^+ , which is partially adsorbed onto the surface of the electrodes of the measuring cell. In this case, the CTA^+ complexes and Br^- ions in the bulk of the liquid crystal are involved in the processes of ionic conduction. The adsorbed CTA^+ cations form monomolecular layers with the long alkyl chains $-(\text{CH}_2)_{15}\text{CH}_3$ directed perpendicular to the electrode surface. This position of the surfactant molecules favors homeotropic orientation of the liquid-crystal molecules.

In the experiments, the temperature of the liquid-crystal cell was set to be 5– 7°C below the temperature of the transition of the $n\text{CB}$ samples from the nematic to isotropic state, and the MB-1 liquid-crystal mixture was studied at $T = 30^{\circ}\text{C}$. For additional control of the initial orientation of the director, the measuring cell with the test sample was placed between the poles of an electromagnet with the field $H = 12$ kOe. The investigations were performed using impedance meters WK 4270 (Wayne Kerr Electronics) and BM 538 (Tesla) operating in the frequency ranges from 50 Hz to 1 MHz and from 1 to 100 MHz, respectively. In the frequency range $0.1 \leq f \leq 50$ Hz, the impedance of the measuring cell with a liquid-crystal sample was measured using an SR830 DSP lock-in amplifier (United States). The ac voltage applied to the electrodes of the cell varied in the range $U_f = 0.1$ – 0.3 V. Simultaneously, the dc bias voltage was also applied to the electrodes and varied in the range $0 \leq U_0 \leq 10$ V. The frequency dependences of the modulus of the impedance $|Z|(f)$ and the phase angle between the current and the voltage $\phi(f)$ were measured. Then, the spectra of the real

component $Z'(f) = |Z|(f)\cos\varphi(f)$ and the imaginary component $Z''(f) = |Z|(f)\sin\varphi(f)$ of the complex impedance were calculated, which made it possible to determine and analyze the behavior of the electro-physical characteristics of the studied samples. The relative error in the impedance measurements did not exceed 5%.

3. FREQUENCY DEPENDENCES OF THE IMPEDANCE OF THE STUDIED SAMPLES

The impedance measurements of liquid dielectrics and electrolytes, including liquid crystals, almost always involve the necessity of separating at least two components of the impedance, one of which is associated with the impedance characterizing the bulk of the sample, whereas the other component is related to the impedance of near-electrode regions of the measuring cell. The impedance in the bulk of the sample is determined not only by the molecular-oriented mesophase of the sample but also by a significant contribution from the electrical conductivity of the liquid crystal, i.e., by the bulk conductivity, which depends on the charge, bulk concentration, and mobility of the ions. The near-electrode impedance is primarily associated with the charge accumulation and motion near the surface of the cell electrodes from the “electrolyte” into the external electrical circuit. The conductivity associated with these phenomena will be referred to as the surface conductivity.

Despite some difference between the electrical conductivity of the liquid-crystal samples 6CB and 7CB, which is provided by ions of incidental impurities, and the electrical conductivity of the samples 8CB and MB-1 doped with the CTAB ionic surfactant, their impedance spectra were very similar to each other. As an example, curves 1 and 2 in Fig. 2 show the frequency dependences of the modulus of the impedance $|Z|(f)$ and phase angle $\varphi(f)$ for the 8CB + CTAB liquid-crystal sample in the absence of dc bias field $U_0 = 0$. The observed nonmonotonic behavior of these dependences is associated with the fact that the changes in the surface and bulk conductivities with variations in the frequency are different in character. It should be noted that the decrease in the modulus of the impedance $|Z|(f)$ (curve 1) and increase in the phase angle $\varphi(f)$ (curve 2) in the frequency range above 1 kHz are typical of frequency dependences of the impedance of conductive materials. These dependences are in good agreement with the frequency dependences of the impedance of a simple electrical circuit consisting of a capacitor C_{lc} and a parallel-connected resistor R_{lc} (see inset in Fig. 2). This impedance is determined by the formula

$$Z(\omega) = R_{lc} \frac{1 - j\omega\tau}{1 + \omega^2\tau^2}. \quad (1)$$

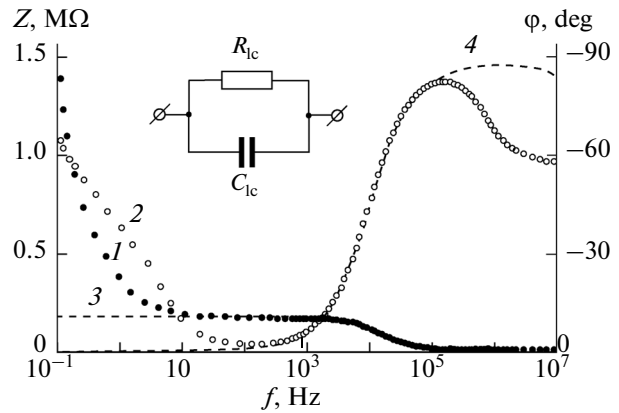


Fig. 2. Frequency dependences of (1) the modulus of the impedance $|Z|$ and (2) the phase angle φ of the 8CB + CTAB liquid-crystal sample. (3, 4) Results of the approximation.

Here, R_{lc} is the bulk electrical resistance of the liquid crystal in the measuring cell, C_{lc} is the capacitance of the cell with the liquid crystal, ω is the circular frequency, and $\tau = R_{lc}C_{lc}$ is the electrical relaxation time.

Curves 3 and 4 in Fig. 2 show the results of the approximation of the experimental dependences for the following parameters of the electrical circuit: $R_{lc} = 1.72 \times 10^5 \Omega$ and $C_{lc} = C_0\epsilon = 96.22 \text{ pF}$, where $C_0 = 6.9 \text{ pF}$ is the capacitance of the empty measuring cell and $\epsilon = 13.8$ is the relative static permittivity of the liquid crystal. The relaxation time in this case is $\tau \approx 1.65 \times 10^{-5} \text{ s}$. As can be seen, the approximation of the measured spectra $|Z|(f)$ and $\varphi(f)$ with the use of fixed values R_{lc} and C_{lc} is applicable only in the frequency range from 0.1 to 100 kHz. It is obvious that, for a more accurate approximation of the results of the measurement at high and ultrahigh frequencies, where the impedance has a capacitive character, it is necessary to take into account the frequency dispersion of the permittivity of the liquid crystal $\epsilon(f)$ [9]. In this case, the capacitance $C_{lc} = C_0\epsilon(f)$ becomes frequency-dependent.

The increase in the impedance and the phase angle φ at low frequencies $f < 100 \text{ Hz}$ is associated with the displacement of positive and negative ions toward the electrodes with opposite signs and with the formation of a thin monomolecular electrical double layer near the electrodes, which is characterized by a high capacitance (Helmholtz layer). Behind this layer, there is a region with a nonequilibrium distribution of ions and neutral molecules (diffusion layer), which diffuse from the electrode into the bulk and back. Since ions in the liquid crystal have a low mobility ($\mu \leq 1 \times 10^{-5} \text{ cm}^2/\text{Vs}$) [10], the processes of charge accumulation near the electrodes, the diffusion of charges, and charge transfer through the liquid crystal–metal electrode interface manifest themselves only at low frequencies $f <$

$(2\pi\tau_i)^{-1}$, where $\tau_i \sim 1.6 \times 10^{-3}$ s is the ion relaxation time. It should be noted that the behavior of the impedance observed at low frequencies is typical of most electrolytes, and the experimentally measured dependences are widely used by researchers for the analysis of the near-electrode processes at the interface [11]. With an increase in the frequency, the impedance of the sample significantly decreases; in the range $f \sim 0.01\text{--}3$ kHz, the modulus of the impedance remains almost constant, and the electric current flowing through the liquid-crystal cell is almost entirely determined by the resistance R_{lc} in the bulk of the liquid crystal. The measurements of the frequency dependences of the impedance of liquid crystals in different frequency ranges make it possible to separate processes that are responsible for the flow of electric current through the sample and that are associated with the near-electrode (surface) and bulk phenomena, as well as to determine the important electrophysical characteristics of the studied liquid crystals, as will be shown below.

Since the electrical resistance in the bulk of the liquid crystal R_{lc} is the active component of the impedance $R_{lc} = Z'(\omega) = |Z|(\omega)\cos\varphi$, it is this resistance that, in the frequency range where $\varphi \approx 0$, determines the oscillating current through the sample, which is in-phase with the ac electric field. The electrical conductivity of liquid crystals, as well as electrolytes, depends on the concentration of ions in the sample so that, with an increase in the concentration of ions, the conductivity first linearly increases, reaches a maximum, and then begins to decrease with decreasing mobility of ions due to the ion–ion interaction. However, for relatively low concentrations of ions, the bulk conductivity of liquid crystals σ_{lc} can be calculated from the resistance R_{lc} and geometrical sizes of the measuring cell (i.e., the surface area of the electrodes S and the gap between the electrodes d) according to the formula

$$\sigma_{lc} = \frac{d}{R_{lc}S} = F \sum_i |z_i| \mu_i c_i = en_0 \alpha (\mu_+ + \mu_-), \quad (2)$$

where F is the Faraday constant, z_i is the charge of the i th ions, c_i is the molar concentration of the i th ions, and μ_i is the mobility of the i th ions. Since the majority of incidental ionic impurities and dissociated CTAB molecular complexes in liquid crystals are monovalent, i.e., $|z_i| = 1$ [12], the resulting conductivity of the liquid crystal can be calculated using the right-hand side of equation (2). Here, e is the electron charge, n_0 is the bulk concentration of CTAB neutral molecules introduced into the liquid crystal, and α is the degree of dissociation of these molecules. The mobilities μ_+ and μ_- correspond to CTA⁺ cations and Br[−] anions.

The mobilities μ_+ and μ_- can be estimated using the relationship between the ionic mobility and the

viscosity of the solution η , which, in the case of liquid dielectrics, has the form [13]

$$\mu = \frac{e}{6\pi r \eta}, \quad (3)$$

where r is the radius of the ion. In the 8CB liquid crystal under the conditions where the ions in an electric field are displaced in the direction of the director, the ionic mobilities were calculated using the following values: the viscosity $\eta = 0.032$ Pa s measured at the temperature $T = 34^\circ\text{C}$ [14, 15], the Br[−] ionic radius $r = 0.196$ nm, and the CTA⁺ ionic radius $r = 0.24$ nm. It turned out that the calculated mobilities $\mu_- = 1.35 \times 10^{-5}$ cm² V^{−1} s^{−1} and $\mu_+ = 1.1 \times 10^{-5}$ cm² V^{−1} s^{−1} are approximately equal to each other.

The bulk concentration of CTAB neutral molecules introduced into the liquid crystal (n_0) can be calculated using the formula [16]

$$n_0 = \frac{N_A v \rho}{M}. \quad (4)$$

Here, N_A is the Avogadro's number, v is the weight concentration of the CTAB surfactant, $\rho \sim 1$ g/cm³ is the density, and $M \approx 291$ g/mol is the molecular weight of the 8CB liquid crystal. For the weight concentration of the CTAB surfactant in the studied sample $v = 0.01$, the calculated bulk concentration of CTAB neutral molecules is $n_0 = 3 \times 10^{19}$ cm^{−3}.

Using the experimentally measured conductivity in the bulk of the 8CB + CTAB liquid crystal $\sigma_{lc} \approx 7.6 \times 10^{-8}$ Ω^{−1} cm^{−1} and the calculated values of the mobility and concentration of CTAB neutral molecules, from the expression (2) it is easy to obtain the degree of dissociation of CTAB molecules $\alpha \approx 0.001$.

It should be noted that, in this calculation, the adsorption of CTA⁺ cations of the surfactant onto the electrodes was ignored, because, in accordance with the data available in the literature, the concentration of adsorbed cations is relatively low and usually does not exceed values in the range from 1×10^{-7} to 1×10^{-8} mol/cm³ [17]. Since the adsorption decreases the concentration of electrically active ions, in order to fit the calculated values to the experimentally measured conductivity σ_{lc} , the degree of dissociation α should be increased by approximately 10%.

Table 1 presents the values of the bulk conductivity of the studied liquid-crystal samples σ_{lc} , bulk concentration of CTAB neutral molecules n_0 , concentration of electrically active ions n_i , their average mobility $\langle \mu \rangle = (\mu_+ + \mu_-)/2$, and the degrees of dissociation α , which were experimentally measured in the absence of dc electric bias field $U_0 = 0$.

As can be seen from Table 1, the electrical conductivities of the liquid-crystal samples 6CB and 7CB are approximately equal to each other and have the same

Table 1. Electrophysical characteristics of the liquid-crystal samples in the absence of an electric bias field ($U_0 = 0$)

Sample	$\sigma_{lc}, 10^{-8} \Omega^{-1} \text{ cm}^{-1}$	$\langle \mu \rangle, 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$	$n_0, 10^{19} \text{ cm}^{-3}$	$n_i, 10^{16} \text{ cm}^{-3}$	α
6CB	2.9	0.9	—	20.0	—
7CB	2.0	1.6	—	7.8	—
8CB + CTAB	7.6	1.1	2.1	4.2	0.001
MB-1 + CTAB	0.15	1.2	1.6	0.51	0.00016

order of magnitude as in the case of the 8CB + CTAB liquid-crystal sample. This coincidence of the conductivities of these liquid-crystal samples is apparently associated with the close values of the average mobilities $\langle \mu \rangle$ and bulk concentrations of ions n_i . A significant decrease in the conductivity of the MB-1 + CTAB sample is associated with the corresponding decrease in the dissociation coefficient of CTAB molecules and in the bulk concentration of ions n_i . It is important to note that the bulk concentrations and average mobilities of ions (Table 1) coincide in order of magnitude with the corresponding values obtained in [12].

4. NEAR-ELECTRODE PROCESSES OF CHARGE ACCUMULATION AND TRANSFER

Theoretical approaches to the investigation and interpretation of the specific features of charge transfer at the electrolyte–contact interface toward the external electrical circuit have been developed for many years [18]. However, the influence of the interface on the behavior of the measured frequency dependences of the electrical conductivity and impedance has been explained using widely accepted methods that consist in constructing equivalent electrical circuits with specific elements providing the required agreement with the experiment for the studied systems [19, 20]. The accumulated experimental experience shows that impedance spectra of electrolytes can be conveniently described using relatively simple equivalent circuits containing conventional resistors and capacitors, as well as a specific frequency-dependent circuit that simulates the processes of diffusion of ions in the system with the Warburg impedance Z_w [19]. This circuit contains frequency-dependent elements connected in series, namely, the active (resistive) R_w and reactive (capacitive) C_w elements:

$$R_w(f) = \frac{W}{\sqrt{2\pi f}}, \quad C_w(f) = \frac{1}{W\sqrt{2\pi f}}. \quad (5)$$

Here, $W = k_f/\sqrt{D}$ is the Warburg constant, which depends on the rate of charge motion near the electrode surfaces k_f and on the ion diffusion coefficient D .

In order to choose the appropriate equivalent circuit containing frequency-dependent Warburg circuit

elements and to determine the optimum values of the circuit elements, it is convenient to represent the experimentally measured impedance spectra $Z(f)$ in the form of a locus of the impedance constructed in the coordinates of the real component Z' and the imaginary component Z'' of the complex impedance. It is obvious that each point in the curve of the locus reflects values of the real and imaginary components of the complex impedance, which are measured at a particular frequency in the range under investigation.

Figure 3 shows the loci of the impedance constructed for the 8CB + CTAB liquid-crystal samples from the results of measurements at frequencies ranging from 0.1 Hz to 10 MHz for different dc bias voltages applied to the electrodes of the measuring cell $U_0 = 0, 2.0, 2.5,$ and 3.0 V (curves 1–4). It can be seen from this figure that the loci of the impedance at high and medium frequencies have nearly the same behavior, and their shape is close to a semicircle. In this frequency range, the locus demonstrates a change in the impedance associated with the bulk of the studied sample, which was considered above. It should be noted that the behavior of the impedance is almost independent of the bias voltage applied to the electrodes of the measuring cell. This is explained by the fact that the 8CB liquid-crystal molecules in the cell are already ordered by the orienting action of the CTAB surfactant in the direction coinciding with the direction of the electric field. The frequency corresponding to the maximum value of Z'' on the semicircle is the relaxation frequency of the measuring cell with the liquid-crystal sample $f_r \approx 11$ kHz. Using this frequency, we can calculate the relaxation time $\tau_r = 1/2\pi f_r \approx 1.45 \times 10^{-5}$ s, which characterizes the relaxation of liquid-crystal molecules in the cell.

At low frequencies ($f < 100$ Hz), there is a radical change in the behavior of the locus of the impedance, which also strongly depends on the dc bias voltage U_0 across the contacts of the measuring. For $U_0 = 0$ (curve 1 in Fig. 3), this segment of the locus has the form of a nearly straight ray. It is this behavior of the locus that is described by the Warburg impedance, the real and imaginary components of which have identical frequency dependences: $\text{Re}(Z_w) = -\text{Im}(Z_w)$. In this case, obviously, the ray of the locus should be inclined at an angle of 45° with respect to the x axis. However, with an increase in the bias voltage U_0 , there occurs a gradual increase in the bending of the low-frequency

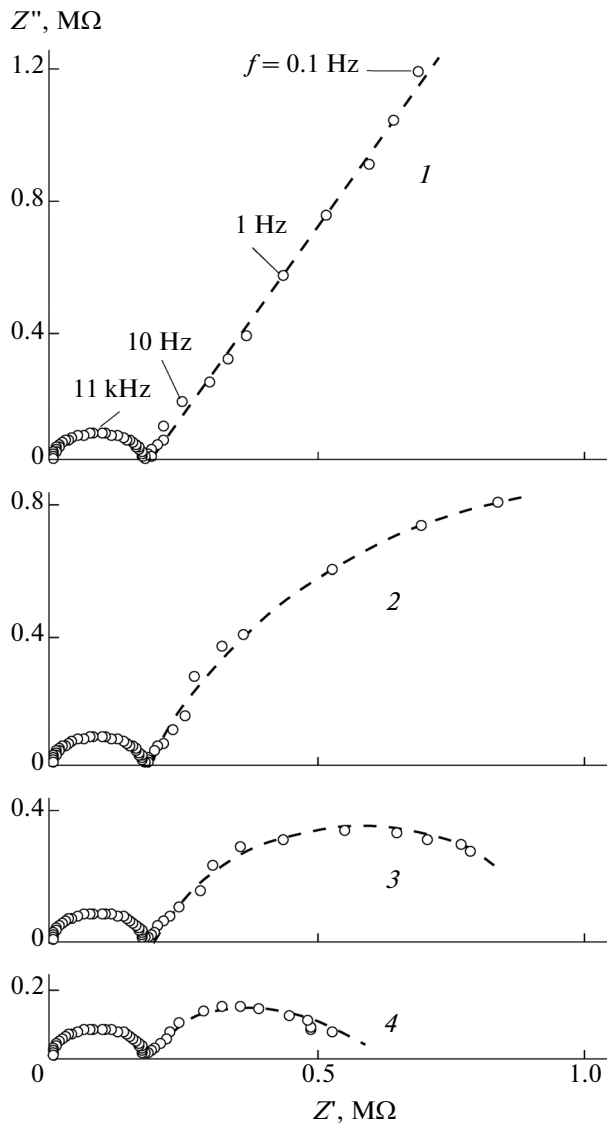


Fig. 3. Loci of the impedance constructed for the liquid crystal 8CB + CTAB at different bias voltages across the contacts of the measuring cell $U_0 = (1) 0$, (2) 2.0, (3) 2.5, and (4) 3.0 V. Dashed lines show the results of the approximation using the equivalent circuit (see Fig. 4).

segment of the locus, which leads to its transformation from the straight line almost into a semicircle (curves 2–4 in Fig. 3). This means that, near the electrodes of the measuring cell, the formation of an electric double layer and the diffusion of ions are accompanied by some additional processes that can be associated with the phenomena of adsorption of the ionic surfactant, injection of charge carriers, or electrochemical reactions with the possible participation of the electrode material. These additional processes should be taken into account in the simulation using an electrical circuit with different combinations of circuits containing resistive–capacitive elements.

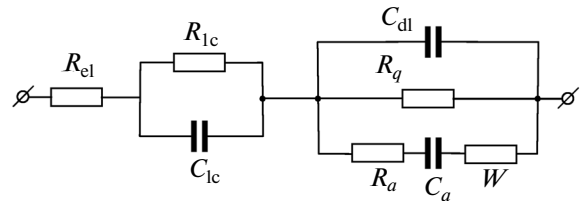


Fig. 4. Equivalent circuit of the measuring cell with a liquid-crystal sample.

In this work, the experimental results were approximated using the specially developed equivalent circuit shown in Fig. 4. Here, the left part of the circuit simulates the resistor with the resistance of the electrodes $R_{el} = 20 \Omega/\square$ and the resistor with the impedance in the bulk of the liquid crystal $R_{lc}C_{lc}$. These elements form a semicircle of the high-frequency part of the locus. The right part of the circuit includes the capacitor with the capacitance of the electric double layer C_{dl} and the resistor with the resistance of charge transfer through the interface R_q , which is connected in parallel with the capacitor C_{dl} . This resistance actually determines the dc electrical conductivity of the liquid-crystal cell. The circuit also includes the capacitor with the capacitance C_a , which simulates the adsorption of CTA⁺ cations on the electrodes, and the resistor with the resistance R_a , which determines the durations of charge and discharge of this capacitor. The Warburg diffusion element W is connected in series with the resistor R_a and capacitor C_a , and this circuit is connected in parallel with the capacitor of the double layer C_{dl} .

For this circuit, the impedance is calculated according to the following equation [19]:

$$Z(j\omega) = R_{el} + (R_{lc}^{-1} + j\omega C_{lc})^{-1} + \{j\omega C_{dl} + R_q^{-1} + [R_a + (j\omega C_a)^{-1} + Z_W]^{-1}\}^{-1}, \quad (6)$$

where the Warburg impedance is given by the expression

$$Z_W = (1 - j)W\omega^{-1/2}. \quad (7)$$

The Warburg constant W is expressed through electro-physical characteristics of the studied sample, such as the surface concentration of ions c_s near the interface of the electrodes and the ion diffusion coefficient D :

$$W = \frac{RTN_A}{F^2 z S \sqrt{2}} \left(\frac{1}{c_s \sqrt{D}} \right), \quad (8)$$

where R is the gas constant, T is the temperature [K], N_A is the Avogadro's number, F is the Faraday constant, S is the surface area of the plates of the measuring cell, and $z = 1$ is the ionic charge. The diffusion coefficient is calculated from the standard formula

Table 2. Nominal parameters of the equivalent circuit elements for the liquid-crystal samples in the absence of an electric bias field ($U_0 = 0$)

Sample	$C_{dl}, 10^{-7} \text{ F cm}^{-2}$	$C_a, 10^{-7} \text{ F cm}^{-2}$	$R_q, 10^7 \Omega$	$W, 10^6 \Omega \text{ s}^{-1/2}$	$D, \text{ cm}^2 \text{ s}^{-1}$
6CB	0.73	6.4	1.8	1.5	1.2×10^{-6}
7CB	2.4	8.2	2.0	1.2	2.6×10^{-8}
8CB + CTAB	3.5	37.0	10.0	0.6	2.7×10^{-7}
MB-1 + CTAB	5.4	9.2	35.0	3.0	5.8×10^{-10}

$$D = \frac{\langle \mu \rangle k_B T}{e} \quad (9)$$

Dashed lines in Fig. 3 represent the results of the approximation of the experimentally measured loci of the impedance $Z''(Z')$ for the 8CB + CTAB sample, which were obtained using expression (6). The electrical parameters of the equivalent circuits and the diffusion coefficients D calculated from formula (9) for all the studied samples are listed in Table 2.

As can be seen from Table 2, the capacitance of the double layer on the interface C_{dl} is of the order of $\sim 1 \times 10^{-7} \text{ F/cm}^2$, which is typical of electrolytes when no electrochemical reactions occur in the near-electrode region. The highest capacitance C_a for adsorption of CTA^+ cations is observed in the 8CB + CTAB liquid-crystal sample. This sample also has the minimum value of the Warburg constant W characterizing the diffusion process. In the absence of bias voltage, the leakage resistance is $R_q \sim 10^7\text{--}10^8 \Omega$, which is several times higher than the resistance in the bulk of the liquid crystal $R_{lc} \sim 1.7 \times 10^5 \Omega$. This difference can be explained by the presence of a potential barrier for the mutual charge exchange between the electrolyte and the metal electrodes.

The results of the approximation have demonstrated that, when the dc bias voltage U_0 is applied to the contacts of the measuring cell, the reactive elements of the equivalent circuits (Fig. 4) for all the studied liquid crystals remain almost unchanged. The observed change in the low-frequency rays of the locus of the impedance with an increase in the dc bias voltage U_0 is associated only with a change in the resistance R_q . As an example, Table 3 shows the depen-

Table 3. Nominal parameters of the equivalent circuit elements for the 8CB + CTAB liquid-crystal sample at different bias voltages U_0

$U_0, \text{ V}$	$C_{dl}, 10^{-7} \text{ F cm}^{-2}$	$C_a, 10^{-6} \text{ F cm}^{-2}$	$R_q, 10^7 \Omega$	$W, 10^6 \Omega \text{ s}^{-1/2}$
0	3.5	3.7	10	0.6
2.0	4.2	3.1	2.0	0.8
2.5	4.9	5.1	0.31	1.4
3.0	5.6	5.6	0.038	1.2

dences of the nominal parameters of the equivalent circuit for the 8CB + CTAB liquid-crystal sample with different dc bias voltages U_0 applied to the contacts of the measuring cell.

It can be seen from Table 3 that, with an increase in the dc bias voltage U_0 , the nominal parameters of the equivalent circuit elements C_{dl} , C_a , and W change only slightly (by a factor of less than two), whereas the resistance R_q decreases by three orders of magnitude. For the maximum voltage U_0 , the resistance R_q almost corresponds to the resistance in the bulk of the liquid crystal $R_{lc} \sim 1.7 \times 10^5 \Omega$. The probable cause for the decrease in the resistance R_q with increasing voltage U_0 can be associated with a decrease in the potential barrier for the mutual charge exchange between the electrolyte and the metal electrodes and, accordingly, with an enhancement of the charge transfer at the electrode–liquid crystal interface.

The absence of the influence of a dc bias field on the capacitance of the electric double layer is typical of many electrolytes. However, the experimentally observed absence of a change in the adsorption capacitance formed by the CTA^+ cations attached to the electrode surface is a non-obvious fact. Apparently, the bonding of surfactant cations with metal electrodes is so strong that it prevents a change in their equilibrium concentration upon application of a dc bias field.

5. CONCLUSIONS

The results obtained in this study have demonstrated that the measured impedance spectra can be used to determine the ionic conductivity in the bulk of liquid crystals doped with ionic surfactants and to investigate the phenomena occurring near the electrode–liquid crystal interface. In particular, the effect of a dc electric field on the electrical and physical characteristics of nematic liquid crystals of the alkyl cyanobiphenyl series and the multicomponent liquid-crystal mixture MB-1, which are doped with ionic surfactants, has been investigated using impedance spectroscopy. The performed approximation of the measured spectra with the specially developed equivalent circuits of the measuring cell with a sample has made it possible to determine the capacitance of the electric double layer and the electrical conductivity of the

samples, as well as the mobility, concentration, and diffusion coefficient of the ions. It has been shown that a region of the space charge is formed in the frequency range $f < 100$ Hz near the electrodes of the measuring cell with a liquid-crystal sample, which leads to an increase in the active and reactive components of the impedance.

It has also been found that, only in the low-frequency range, the impedance spectra depend substantially on the dc bias voltage applied to the sample, which leads to a significant increase in the electrical conduction through the liquid crystal–metal electrode interface. The reason for this effect is most likely associated with a decrease in the potential barrier that prevents the mutual exchange of charges between the liquid crystal and the metal electrodes. However, the capacitance of the electric double layer and adsorption capacity are almost independent of the electrode material and remain unchanged when dc electric bias fields are applied to the sample. This fact indicates that the CTAB cations adsorbed on metal electrodes are very strongly bound to the surface of the contacts, so that their concentration does not change even in extremely strong electric fields.

ACKNOWLEDGMENTS

This study was supported by the Siberian Branch of the Russian Academy of Sciences (integration project no. 109).

REFERENCES

1. Ya. Barton' and A. A. Kal'nin, *Tech. Phys.* **43** (1), 112 (1998).
2. I. R. Gural'nik and S. A. Samagin, *Kvantovaya Elektron. (Moscow)* **32** (4), 362 (2002).
3. L. M. Blinov, E. I. Kats, and A. A. Sonin, *Sov. Phys.—Usp.* **30** (7), 604 (1987).
4. L. Komitov, B. Helgee, J. Flix, and A. Matharu, *Appl. Phys. Lett.* **86**, 023502 (2005).
5. V. G. Chigrinov, V. M. Kozenkov, and H.-S. Kwok, *Photoalignment of Liquid-Crystalline Materials: Physics and Applications* (Wiley, New York, 2008).
6. P. Pagliusi and G. Cipparrone, *J. Appl. Phys.* **92** (9), 4863 (2002).
7. V. Ya. Zyryanov, M. N. Krakhalev, and O. O. Prishchera, *Mol. Cryst. Liq. Cryst.* **489**, 273/[599] (2008).
8. T. V. Bezrodnaya, V. V. Nesprava, G. A. Puchkovskaya, I. T. Chashechnikova, Yu. P. Boiko, and Ya. Baran, *J. Appl. Spectrosc.* **78** (1), 50 (2011).
9. B. A. Belyaev, N. A. Drokin, V. F. Shabanov, and V. N. Shepov, *Phys. Solid State* **45** (3), 598 (2003).
10. M. G. Tomilin, *Interaction of Liquid Crystals with the Surface* (Politekhnik, St. Petersburg, 2001) [in Russian].
11. N. G. Bukun and A. E. Ukshe, *Russ. J. Electrochem.* **45** (1), 11 (2009).
12. S. Naemura and A. Savada, *Mol. Cryst. Liq. Cryst.* **400**, 79 (2003).
13. A. I. Zhakin, *Phys.—Usp.* **46** (1), 45 (2003).
14. P. Patricio, C. R. Leal, L. F. V. Pinto, A. Boto, and M. T. Cidade, *Liq. Cryst.* **39**, 25 (2012).
15. W. Martienssen and H. Walimont, *Springer Handbook of Condensed Matter and Materials Data* (Springer-Verlag, Berlin, 2005).
16. M. F. Grebenkin and A. V. Ivashchenko, *Liquid-Crystal Materials* (Khimiya, Moscow, 1989) [in Russian].
17. M. Halder, *Chem. Educ.* **12**, 33 (2007).
18. B. B. Damaskin, O. A. Petrii, and G. A. Tsirlina, *Electrochemistry* (Khimiya, Moscow, 2006) [in Russian].
19. B. M. Grafov and E. A. Ukshe, *Usp. Khim.* **XLIV** (11), 1979 (1975).
20. J. R. Macdonald, *Ann. Biomed. Eng.* **20**, 289 (1992).

Translated by O. Borovik-Romanova