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CLUSTER STRUCTURE OF THE NEAR-ELECTRODE LAYER IN LIQUID DIELECTRICS

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A method for determining the characteristics of charge clusters in low-conductivity liquids and an experimental setup for its realization are proposed. From the experimental results an inference about the molecular structure of the contact layer has been drawn.

Necessary Theoretical Information. The study of the contact layer of metal–liquid dielectric is one of the main problems of electrodynamics [1]. The molecular structure of this layer is not understood so far and, at the moment, it is only known that it represents an aggregation of charge clusters at the electrodes [2, 3]. In this work we present results of an investigation of this structure by the method of measuring the angle of rotation of the plane of polarization of light transmitted by the dielectric. The method is based on the fact that in an electric field the migration of clusters to the electrodes and their polarization turn the initially isotropic dielectric into an anisotropic dielectric with the optical axis parallel to the electric field. For plane parallel electrodes and a constant electric field directed along the z axis, the tensor of dielectric permittivity of such a medium has the form

$$\hat{\varepsilon} = \begin{pmatrix} \varepsilon_0\varepsilon_1 & 0 & 0 \\ 0 & \varepsilon_0\varepsilon_1 & 0 \\ 0 & 0 & \varepsilon_0\varepsilon_2 \end{pmatrix} . \qquad (1)$$

When light is transmitted by the medium considered, birefringence appears and its plane of polarization rotates. The angle of rotation φ of the plane of polarization of linearly polarized light traversing a distance l perpendicular to the z axis in this medium is determined by the well-known relation

$$\varphi = \frac{\pi l}{\lambda} \sqrt{\mu} \, (\sqrt{\varepsilon_2} - \sqrt{\varepsilon_1}) \, . \qquad (2)$$

As experiments show [3], in dielectric liquids the quantities ε_1 and ε_2 are usually close in value. Therefore, assuming that $\mu \cong 1$, in place of relation (2) we can use the approximate formula

$$\varphi = \frac{\pi l}{2\lambda} \frac{\Delta\varepsilon}{\sqrt{\varepsilon_1}} \ (\text{rad}) \, , \qquad (3)$$

where $\Delta\varepsilon = \varepsilon_2 - \varepsilon_1$.

The quantity ε_1 depends on the composition of the dielectric liquid (the concentration of a polar electrolytic impurity in a nonpolar solvent) and can be measured in the process of its preparation. Since the degree of dissociation of impurities is very small, $\alpha_{\text{d.imp}} \sim 10^{-8}$, and the relative change in their concentration at the electrodes can be neglected, the value of ε_1 can be assumed to be constant throughout the interelectrode gap.

The quantity $\Delta\varepsilon$ depends on the polarization of the charge clusters in the constant electric field of the electrodes and is calculated by the Debye–Langevin formula

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$$\Delta\varepsilon = n\frac{NP^2}{3\varepsilon_0 kT}. \tag{4}$$

Thus, for φ the following expression is true:

$$\varphi = \frac{l\pi nNP^2}{6\lambda\sqrt{\varepsilon_1}\,\varepsilon_0 kT}. \tag{5}$$

Formula (5) allows one to determine the product nN from a known value of φ. Then, to determine N, it is necessary to specify n, which can be done using data of [4, 5]. Namely, from the expression for the partial density of the cluster-ion current [5]

$$j = Z\,e\,b\,n\,E - (Zn)'\,De = Z_0 e\,b\,n_0 E_0\,, \tag{6}$$

it follows that

$$\left(\frac{Zn}{Z_0 n_0}\right)\frac{E}{E_0} - \frac{\varphi_*}{E_0}\left(\frac{Zn}{Z_0 n_0}\right)' = 1\,, \quad \varphi_* = \frac{D}{b}\,, \qquad r\left(\frac{Zn}{Z_0 n_0}\right)' - \frac{E}{E_0}\left(\frac{Zn}{Z_0 n_0}\right) = -1\,,$$

$$\frac{\partial}{\partial\xi}\left(\frac{Zn}{Z_0 n_0}\right) - \frac{E}{E_0}\left(\frac{Zn}{Z_0 n_0}\right) = -1\,, \tag{7}$$

where $r = \varphi_*/E_0$; $\xi = z/r$; z is the coordinate directed along the field.

Equation (7) has the exact solution

$$\frac{Zn}{Z_0 n_0} = \exp(F)\left\{1 + \frac{E}{E_0}\int_{\xi}^{\frac{d}{2r}} \exp(-F)\,d\xi\right\} = 1\,, \tag{8}$$

$$F = \int_{\xi}^{\frac{d}{2r}} \frac{E}{E_0}\,d\xi\,, \quad Z_0 n_0 = \alpha_{\text{d.imp}} N_{\text{imp}}\,, \tag{9}$$

where $\alpha_{\text{d.imp}}$ and N_{imp} are the degree of dissociation and the concentration of the dissociating impurity in the basic liquid.

The function $E(\xi)$ can be determined experimentally by the method described in [6], after which the product Zn is represented as a function of E_0 and ξ:

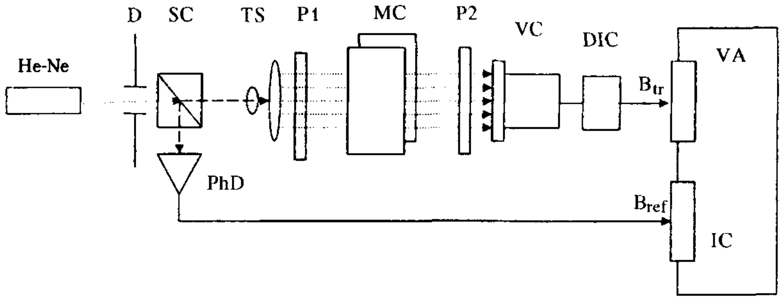
$$Zn = IZ_0 n_0 = f(E_0, \xi)\,. \tag{10}$$

Since, according to [4], Z is related to N by the relation

$$R_c = 0.7\left(\frac{ZeP}{\varepsilon_0\varepsilon_1 kT}\right)^{1/2} = LN^{1/3}\,, \tag{11}$$

considering relations (5), (10), and (11) as a system of equations, we obtain:

the mean number of molecules in a cluster



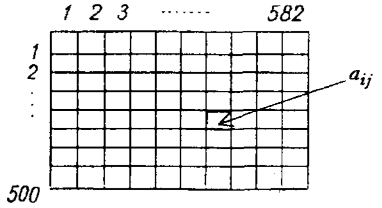


Fig. 1. Schematic diagram of the experiment on the spatial distribution of the angle of rotation of the plane of polarization φ.

Fig. 2. Matrix of resolution of a video-signal frame.

$$N \approx \left(\frac{6\lambda \varepsilon_0^2 \varepsilon_1^{3/2} k^2 T^2 L^2 \varphi}{\pi l e P^3 f} \right)^3, \tag{12}$$

the mean charge number of a cluster

$$Z \approx \frac{2\varepsilon_0 \varepsilon_1 k T L^2 N^{2/3}}{eP}, \tag{13}$$

the concentration of clusters

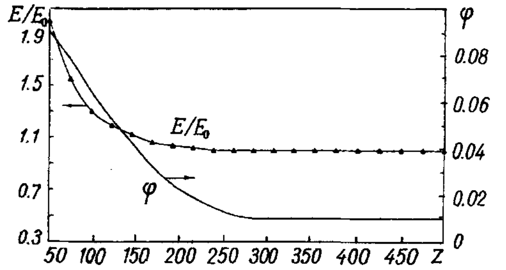
$$n \approx \frac{f}{Z}. \tag{14}$$

Relations (12)-(14) are the calculation formulas of the experiment.

Experimental Procedure. Linearly polarized light of an He–Ne laser (LGN-222) (see Fig. 1) transmitted by a diaphragm (D) is divided by a beam-splitting cube (SC) into two beams: a reference beam (B_{ref}) and a transmitted beam (B_{tr}). The instantaneous output power of the laser is controlled by a photodetector (PhD) using the reference beam. The object beam broadened by a telescopic system (TS) to the cross section of the measuring cell (MC) passes parallel to the cell electrodes. The rotation of the plane of polarization of the object beam upon application of a static electric field to the experimental cell with the investigated liquid causes a change in the intensity of the luminous flux. Quantitative estimation of the luminous-flux intensity is performed by a video camera (VC) (MSF-468) whose objective lens is chosen so that the interelectrode gap occupies the entire frame. Polarizers P1 (polarizer) and P2 (analyzer) perform calibration of the data at the output of the video camera. To enhance the resolution of the setup with respect to a angle of rotation, a device for increasing the contrast range (DIC) is used [7].

The analog data from the photodetector PhD and the video camera VC are converted to a digital code by an input card (IC) and a video adapter (VA) installed in a Pentium 150 computer. Synchronization of the data recording is performed by programs. The software of the video adapter VA makes it possible to record an image continuously and in the stop-frame regime. In processing the measurement results, a video frame is transformed into a matrix a_{ij} (500 × 582) of pixels by the 8-digit analog-to-digital converter of the video adapter VA (see Fig. 2). Each element of the matrix (pixel) represents a photosensitive element whose output current intensity depends on its illumination.

For the purpose of determining the actual geometric size of an element of the matrix a_{ij} and taking into account the geometric distortions of the objective lens, a plate with a marked 0.1-mm standard grid is set in the interelectrode gap of the measuring cell (perpendicular to the electrodes). The caliber file obtained makes it possible to determine the geometric size of objects in the interelectrode gap by programs and to allow for



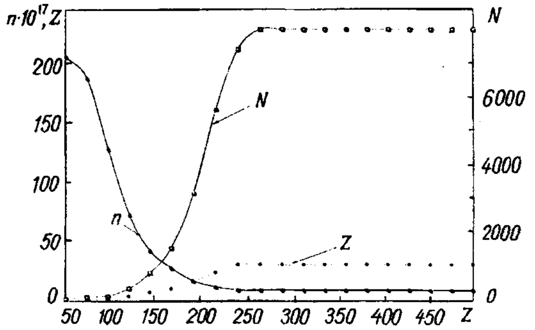


Fig. 3. Spatial distribution of φ and the dimensionless electric-field strength E/E_0 ($z = 0$ μm corresponds to the positive electrode) for a solution of butyl alcohol in heptane. φ, deg; z, μm.

Fig. 4. Dependence of the mean number of molecules in a cluster N, the mean charge number Z, and the concentration of clusters n on the coordinate z for a solution of butyl alcohol in heptane.

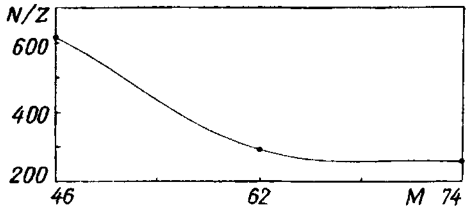


Fig. 5. Dependence of the ratio N/Z for solutions with a different molar mass of the polar additive. M, g/mole.

the geometric distortions of the objective lens. For each investigated liquid, in the absence of an electric field, we recorded a reference frame $I_{\mathrm{ref}(ij)}$ (the matrix of the elements a_{ij}). A change in the angle φ causes a change in the amplitude of the light and the amplitude of the current $I_{\mathrm{tr}(i,j)}$. According to the Malus law,

$$I_{\mathrm{tr}(i,j)} = I_0 \cos^2 \varphi_{(i,j)} \,. \tag{15}$$

From expression (15), we determine the value of φ for each element of the matrix a_{ij} and, as a result, obtain a two-dimensional spatial distribution of φ throughout the interelectrode gap:

$$\varphi_{(i,j)} = \arccos \sqrt{\left(\frac{I_{\mathrm{tr}(i,j)}}{I_0}\right)} \,. \tag{16}$$

The distribution of the angle of rotation φ combined with an analogous distribution of E/E_0 obtained by the procedure of [6] makes it possible to calculate N, Z, and n by formulas (12)-(14).

Results of Measurements. Results of experimental measurements of the spatial distribution of the angle φ and the dimensionless electric-field strength E/E_0 obtained for a 10% solution of butyl alcohol in heptane (E_0 = 400 V/cm) are presented in Fig. 3.

Results of calculating the spatial distribution of N, Z, and n are presented in Fig. 4. Results of a comparison of maximum values of N and Z determined for different liquids as functions of the molar mass of polar additive, are presented in Table 1 and Fig. 5.

The results of the experiment performed (Fig. 4) showed that in the contact layer of low-conductivity liquids, the size of the clusters, their concentration, and the charge number change. Namely, away from the electrodes, from a distance of 30–50 μm the mean number of polar molecules in a cluster begins to increase (from ten molecules to several thousand) with a simultaneous increase in the charge number of the clusters

TABLE 1. Basic Characteristics of the Charge Clusters for the Investigated Solutions (polar additive in heptane)

Active polar additive (content of alcohol in % by volume)	M of active polar additive	N	Z
Ethyl alcohol (10%)	46	34,480	56
Butyl alcohol (10%)	74	7920	31
Ethylene glycol (5%)	62	21,180	73

(from one to several tens of ions) and decrease in the concentration of the clusters (from 10^{19} to 10^{17} clusters in 1 m^3). The indicated changes occur in a layer ~300 μm wide. The steady-state characteristics of the charge clusters depend on the kind of polar impurity in the basic liquid (see Fig. 5 and Table 1): as M of the additive increases, the ratio of the mean number of molecules to the charge number of the clusters decreases.

From the results obtained and the results of [2-5] it may be concluded that the molecular structure of the contact layer in low-conductivity liquids consists of a dense part (~20 μm) immediately adjacent to the electrode and a loose part (~300 μm). In the dense part ionic conduction with charge carriers corresponding in size to an ionized molecule predominantly occurs, and in the loose part, cluster conductivity with clusters variable in size and charge number is predominantly realized. Here, the mean number of molecules in one cluster increases to several thousand with a simultaneous increase in the charge number to several tens of ions. In the contact layer as a whole we observe layer-by-layer molecular ordering in the direction perpendicular to the electrode.

NOTATION

$\hat{\varepsilon}$, tensor of dielectric permittivity; ε_0, dielectric constant; ε, relative dielectric permittivity of the medium in the directions x and y; ε_z, relative dielectric permittivity of the medium in the z direction; l, distance traveled by linearly polarized light perpendicular to the x axis; φ, angle of rotation of the plane of polarization of the light; μ, relative magnetic permeability of the medium; λ, wavelength of the light in vacuum; N, mean number of polar molecules in one cluster; P, dipole moment of a polar molecule; k, Boltzmann constant; T, absolute temperature; D, diffusion coefficient; d, distance between the electrodes; b, cluster mobility; E, electric-field strength; E_0, mean electric-field strength; n, concentration of the charge clusters; n_0, concentration of the clusters away from the electrodes; Z, local value of the charge number of the clusters; Z_0, charge number of the clusters away from the electrodes; R_c, mean radius of the dense part of a cluster; L, mean length of the dipole of a polar impurity molecule; $I_{\mathrm{tr}(i,j)}$, intensity of the current at the output of the element a_{ij} as the angle φ changes; $I_{\mathrm{ref}(i,j)}$, intensity of the current at the output of the element a_{ij} of the reference frame; I_0, amplitude of the current in the absence of voltage across the electrodes; e, electron charge; M, molar mass. Subscripts: imp, impurity; d, dissociation; c, cluster; tr, transmitted; ref, reference.

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