CHARACTERISTICS OF THE MOLECULAR STRUCTURE OF WEAKLY CONDUCTING LIQUIDS IN AN ELECTRIC FIELD

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It is found experimentally that synergetic specific features displayed by weakly conducting liquids in an electric field consist in their cluster (locally ordered) structure, which is achieved due to the charged associates of admixture molecules bound with one another by hydrogen bonding.

Problems of the synergetic nature of weakly conducting liquids suggested themselves when studying the properties of electric convection, which are of great importance for designing heat-and mass-exchange systems operating in weightlessness. In its cellular form, the electric convection of weakly conducting fluids resembles Bernard's thermal convection, but in contrast to the latter, it depends on the distribution of Coulomb forces acting on the space charge of the liquid [1]. At the observed degrees of dissociation of electric impurities in weakly conducting liquids for each ion there are no fewer than $10^6 - 10^8$ molecules of the liquid. These complexes, called "charge clusters" [2], change the molecular structure of the liquid. We recorded this change by the methods of x-ray structural analysis [3] and infrared spectroscopy [4].

We carried out investigations on solutions of butyl alcohol in transformer oil, varying the concentration of the impurity in the main liquid and the voltage across the plane-parallel electrodes.

In carrying out the x-ray structural analysis (Fig. 1), we used a DRON 2 general purpose x-ray diffractometer to fix the intensity of x-ray radiation (CuK_α filtered) scattered by the front electrode of the cuvette. The electrode was made of a thin metal foil (0.01 mm), allowing x-rays to partially penetrate the cathode sheath and give information about its structure. On x-ray photographs of the liquids investigated (Fig. 2) we discovered a halo characteristic for media with locally ordered microregions (there were no other modulations of the background and selective reflections). The half-width of the halo is connected with the effective dimensions of the regions of local ordering:

$$L = \frac{\lambda}{\Delta \cos \vartheta_{max}},$$ (1)

whereas its position is connected with the most frequently encountered interatomic (intermolecular) distance in these regions:

$$r_{max} = \frac{1.23}{S_{max}}, \quad S = \frac{2 \sin \vartheta}{\lambda}.$$ (2)

Studying the position of the maximum and the half-width of the halo and varying the concentration of the impurity and the voltage across the electrodes, it is possible to reveal the specific features of the molecular structure of the liquids investigated. In addition to the analysis we calculated the functions of the radial distribution of the atomic density or correlation functions from the formula

$$W(r) = 2\pi r^2 [\rho(r) - \rho_0] 8\pi r \int_{S_1}^{S_2} \frac{I(S) - f^2(S)}{f^2(S)} S \sin 2\pi Sr \, dS,$$ (3)
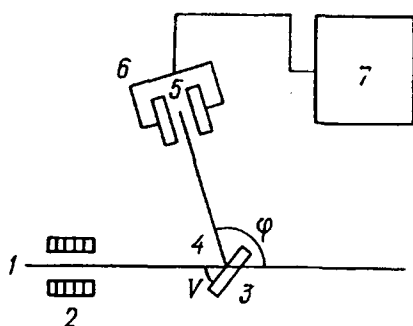
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Fig. 1. Scheme for obtaining an x-ray diffractogram: 1) primary beam, 2) collimator slit, 3) sample, 4) axis of rotation of sample and counter, 5) inlet slit of counter, 6) counter, 7) unit for electronic processing of counter signals.
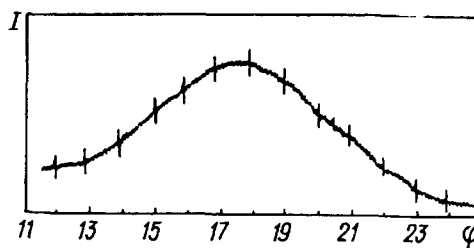
Fig. 2. A fragment of x-ray photograph of butyl alcohol solution in transformer oil. I, rel. units; φ, deg.

TABLE 1. Dependence of Intermolecular Distance in Cathode Sheath of Weakly Conducting Liquid on Impurity Concentration and Voltage Across Electrode

U, kV	C, %				
	0	1	5	10	20
+5	9.20/5.92	9.25/5.84	9.30/5.86	9.30/5.86	9.30/5.86
0	9.20/5.92	9.20/5.92	9.25/5.89	9.25/5.89	9.25/5.89
−5	9.15/5.96	9.15/5.96	9.15/5.96	9.15/5.96	9.15/5.95

Note: φ in the numerator, r_m in the denominator.

where $f(S)$ are the atomic amplitudes of scattering taken from the tables of [5]. Our measurements showed that the weakly conducting liquids investigated are characterized by the presence of ordered microregions with effective dimensions of about 100 Å. Table 1 lists the values of the most frequently encountered interatomic distance in these regions depending on the concentration of the impurity and voltage on the front electrode. It is seen from the table that the most frequently encountered intermolecular distance in ordered microregions r_m in the absence of an electric field is equal to 5.92 Å at small (~1%) concentrations of the impurity in the main liquid and to 5.89 Å at large (5% and above) concentrations of the impurity. The appearance of an electric field in the liquid additionally changes this distance to the decreasing side (5.86 Å) on the anode and the increasing side (5.96 Å) on the cathode.

The data obtained are confirmed by distributions of correlation functions that have three maxima for the liquids investigated: at 1.8 Å, 6.0 Å, and 10.2 Å. The first maximum corresponds to the distance between the atoms of carbon; the second, between the alcohol molecules; and the third, between the molecules of the oil. The second maximum undergoes a substantial change, testifying to the formation of associates of the impurity molecules (alcohol) in the main liquid. This conclusion was also confirmed by IR spectroscopy of the liquids investigated.

The IR spectra were recorded on a Specord 75 IR spectrophotometer in the range of wave numbers of from 4000 to 400 cm^{-1}. We placed the liquids in specially made cuvettes whose windows were made of IR-transparent materials used simultaneously as electrodes (NaCl, CaCl). The absorption spectrum obtained for pure transformer oil on specimens of capillary thickness (30 μm) is shown in Fig. 3. In the spectrum we identified the 2810–2920 cm^{-1} (stretching vibrations of C–H atoms in the CH_2 and CH_3 groups, 1410–1320 cm^{-1} (deformation vibrations of the CH_2 and CH_3 groups), 1200, 1040, 970 cm^{-1} (stretching vibrations of C–O and C–C atoms), 750 cm^{-1} (rocking vibrations of the CH_2 groups).

In spectra of thick specimens (1–5 mm), the baunds 2400 and 1800–1900 cm^{-1} characteristic of hydrocarbons with C=C and C=O bonds are distinquished additionally. Their concentration in the transformer oil is small.
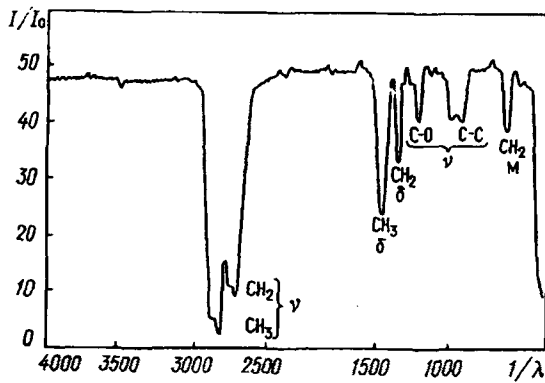
Fig. 3. The absorption spectrum of pure transformer oil. I/I_0, %; $1/\lambda$, cm^{-1}.
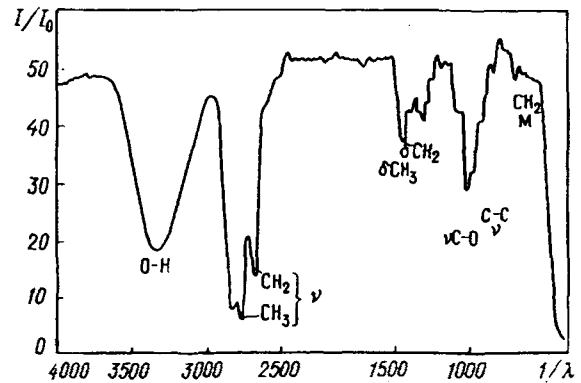
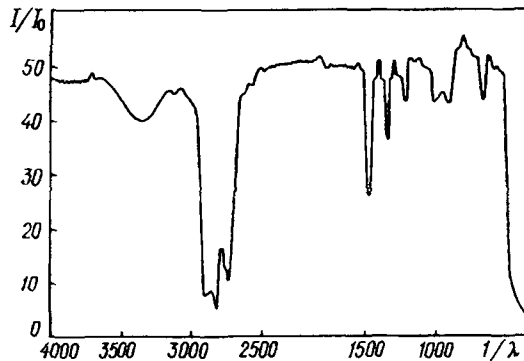Fig. 4. The absorption spectrum of butyl alcohol.

Fig. 5. The absorption spectrum of a 20-percent solution of butyl alcohol in transformer oil.

TABLE 2. Position of Absorption Band of O–H Atoms with Hydrogen Bond with Variation of Impurity Concentration and Voltage Across Electrodes

U, kV	C, %				
	0	1	5	10	20
0	3300	3300	3305	3310	3310
500	3300	3305	3310	3310	3310

The spectrum of butyl alcohol (Fig. 4) consists of the bands: 3310 cm^{-1} (vibrations of the O–H atoms having a hydrogen bond) and 2940–2850 cm^{-1} (symmetric and asymmetric vibrations of C–H atoms in the CH_2 and CH_3 groups).

The bands of deformation, torsional, and stretching vibrations of the CH_2, CH_3, C–O, and C–C groups are located in the long-wave region. The spectra of the butyl alcohol solutions in transformer oil contain all the bands typical of each of the substances separately (Fig. 5). This indicates that there is no chemical bond between the molecules of the impurity and solvent. The impurity concentration and electric field strength influence only the position and intensity of the 3310 cm^{-1} band (vibrations of the O–H molecules having a hydrogen bond). Our measurements showed that the Beer law holds and the coefficients of hydrogen bonds are constant for high concentrations (10%, 15%, and 20%) and that this is indicative of the fact that the alcohol molecules form strong associates with one another. As the concentration decreases (to 2% and lower) the 3310 cm^{-1} band decreases and shifts to the side of smaller energies (Table 2). This indicates decomposition of the associates of the alcohol molecules into dimers and monomers without forming bonds with the molecules of the main liquid.

The appearance of an electric field in the liquid is equivalent to an increase in the concentration of impurity. It shifts the 3310 cm^{-1} band to the side of larger energies. This can be caused by the associates of the alcohol molecules accumulating near the electrodes and by the ordering of the molecular medium in the contact layer.

The results of both experiments agree qualitatively with each other and confirm the assumption that the conductivity of insulating liquids has an ion-cluster character, i.e., it is realized by the charged associates of the impurity molecules formed due to the hydrogen bonds of molecules with one another. Near the electrodes, the charge clusters form layer-by-layer ordered molecular structures the mean distance in which decreases on the anode due to a denser packing of molecules in the charge clusters and increases on the cathode due to the disordering effect on the cluster layer of the injected flux of free oppositely charged ions (in the media considered the charge injection is directed from the cathode). Injection of a charge inside the interelectrode space is also very peculiar. Being realized by charged microregions with transverse dimensions of the order of 100 Å, it becomes similar to the injection of drops that separate from a free charged surface and cause convection of the remaining liquid.

NOTATION

Δ, half-width of halo; L, effective dimension of region of local ordering; λ, x-ray radiation wavelength; ϑ_{max}, position of halo maximum; r_{max}, interatomic (intermolecular) distance; r_m, mean intermolecular distance; $W(r)$, correlation function; $\rho(r)$, atomic density; ρ_m, mean atomic density; $f(S)$, atomic amplitudes of scattering; S_1 and S_2, limits of x-ray photograph fragment investigated; C, concentration of impurity; I, intensity of x-ray radiation; U, voltage across electrodes; φ, diffraction angle; I/I_0, relative intensity of transmited IR-radiation.

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