

## SOME PROPERTIES OF THE CONTACT OF METALS WITH LIQUID DIELECTRICS

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*Results of an experimental study of regularities in the formation and conductivity of adsorbed near-electrode layers on electrodes in weakly conducting liquids are reported.*

Unlike the well-studied contacts of metals with solid dielectrics, semiconductors, or electrolytes, the contact of metals with liquid dielectrics has long remained unnoticed by investigators. This is explained partly by the difficulties encountered in describing the nonlinear electrohydrodynamic (EHD) effects occurring in these media in the presence of an electric field [1] and partly by problems arising in simultaneous recording of the electric current and convection of liquids in the range of low (up to  $10^3$  V/m) electric-field intensities. Nevertheless, the fact that the EHD effects show much promise for heat- and mass-transfer systems under zero-gravity conditions as well as in systems of micromechanics and adaptive optics make investigations of this contact urgent. The main aspect in such investigations is regularities in the processes of formation and conductivity of adsorbed near-electrode layers on electrodes in weakly conducting liquids.

In the present work these investigations have been conducted for the first time simultaneously by three independent methods, namely, the method of pulsed volt-ampere characteristics (VAC), the microwave-probing technique, and the method of holographic interferometry.

The first method (its measurement procedure is described in [2]) makes it possible to determine the time of formation and width of adsorbed near-electrode layers, to evaluate the concentration and mobility of charge carriers in each layer (at an anode and a cathode), and to construct volt-ampere characteristics of the layers starting from low (1 V/m) electric intensities. The second technique [3] complements the first method in the range of moderate prebreakdown ( $10^4$ – $10^6$  V/m) electric intensities. The third method (see [4]) monitors the refractive index and convection of a liquid when performing measurements by the first two methods.

In the experiments, use was made of a standard series of metals (In-Cr) as electrode materials whose vacuum electronic work function ( $A_w$ ) varied from 3.8 to 4.6 eV; butyl alcohol (BA) solutions in transformer oil (TO) as weakly conducting liquids; and a system of changeable plane-parallel electrodes as experimental cuvettes.

As measurements performed by the pulsed VAC method have revealed, in weakly conducting liquid media on the surface of submerged electrodes following the formation of monomolecular double electric layers during electronic polarization of molecules ( $\sim 10^{-12}$  sec) narrow (up to 0.02 mm) adsorbed layers are formed near the electrodes over a period of 100–200  $\mu$ sec after applying voltage to the latter. These layers possess an elevated (by 2–3 orders of magnitude) conduction and dielectric permittivity (by 30–40%).

The volt-ampere characteristics of the adsorbed layers (Fig. 1) correspond to Ohm's law, but unlike it, a linear relation between the electric current across the electrode surface ( $I_{sur}$ ) and the voltage applied to the layer ( $U_{sur}$ ) exists only up to some threshold voltage ( $U_{th}$ ), below which the current decreases abruptly (exponentially) and becomes lower than the sensitivity of the installation ( $10^{-10}$  A). It has been found that these  $U_{th}$  values are independent of low-voltage conduction ( $\sigma$  of the liquid and an interelectrode distance but depend on a material of the electrodes and their polarity (Fig. 2). Despite its low value ( $\sim 10$  mV),  $U_{th}$  initiates a considerable intensity of the electric field between the "plates" of a double electric layer, since it is applied at a distance equal to, approximately, of one molecule. Indeed, since

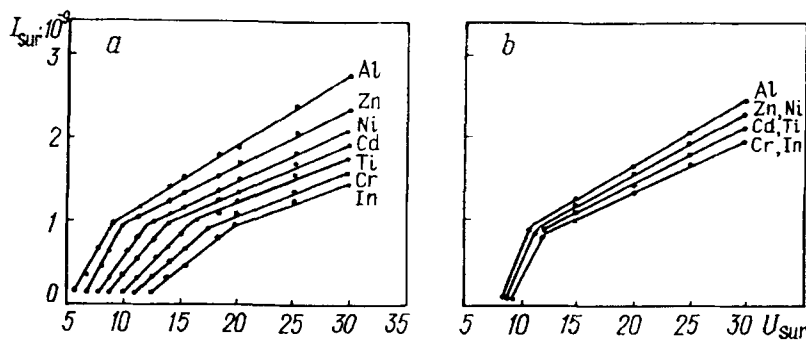


Fig. 1. Volt-ampere characteristics of near-electrode layer on varying the electrode material (a) cathode, b) anode). BA solution in TO (1%), the interelectrode gap is 2 mm, the investigated electrode area is 1 cm<sup>2</sup>.  $I_{sur}$ , A;  $U_{sur}$ ,  $\mu$ V.

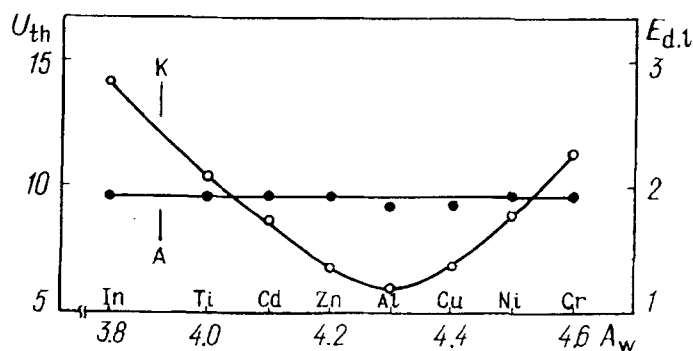


Fig. 2. Threshold voltage and threshold electric intensity in a double electric layer versus the electrode material (the same conditions as in Fig. 1).  $U_{th}$ ,  $\mu$ ;  $E_{d.l}$ ,  $\mu$ V/cm;  $A_w$ , eV.

$$E_{d.l} \approx \beta \frac{U_{th}}{\delta}, \quad (1)$$

where  $\delta$  is the distance from the adsorbed molecule to the electrode and  $\beta$  is the field gain at the microedges, in our case ( $\delta \sim 5\text{\AA}$ ,  $\beta \approx 10-100$ ) this gives  $E_{d.l} \approx 10^8-10^9$  V/m, which is quite sufficient for emission of the electrode material. Qualitatively, this dependence is shown in Fig. 2. The difference between the anode and cathode processes is explained by the fact that on the cathode as a result of the reducing reaction contact of the liquid with "pure" metals takes place, which allows manifestation of their emission properties; on the anode, due to the oxidation reaction contact with the metal oxide films masking these properties occurs. The extremum at 4.2 eV corresponds to easier travel of an electron from the electrode material to the hydrocarbon organic matter. The mobility of charge carriers in adsorbed layers corresponds mainly, with respect to its value ( $10^{-6}-10^{-7}$  m<sup>2</sup>/(V·sec)), to the ionic conductivity of the layers, which together with the presence of a potential barrier ( $U_{th}$ ) testifies once again to the dissociation-injection mechanism of their occurrence due to electrochemical reactions on the electrodes.

Further investigations of the near-electrode layers by microwave probing have revealed that in addition to the above transition processes, a slow (for  $\sim 20$  min) build-up of the width of the adsorbed layers occurs near the electrodes. The considerable difference in the characteristic times of emergence and build-up of an adsorbed layer (by 5-6 orders of magnitude) is attributed to the lower (by 2-3 orders) mobility and concentration of charge carriers (charge clusters) in the main liquid as compared to the mobility and concentration of charge carriers in the layer (of ions).

The maximum width of the layers depends on the voltage across the electrodes and the impurity concentration (low-voltage conduction of the liquid). The corresponding dependences for the layers formed for  $\sim 30$  min are shown in Fig. 3.

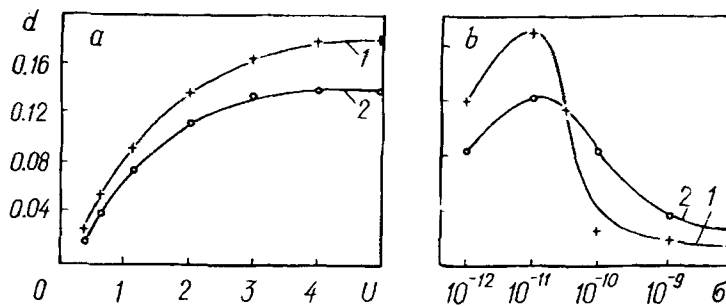


Fig. 3. Maximum thickness of near-electrode layers versus voltage across electrodes (a) and low-voltage conduction of interelectrode gap (b) (copper electrodes, BA solution in TO (1%),  $t = 30$  min): 1) near-anode layer; 2) near-cathode layer.  $d$ , mm;  $U$ , kV;  $\sigma$ ,  $\Omega^{-1} \cdot m^{-1}$ .

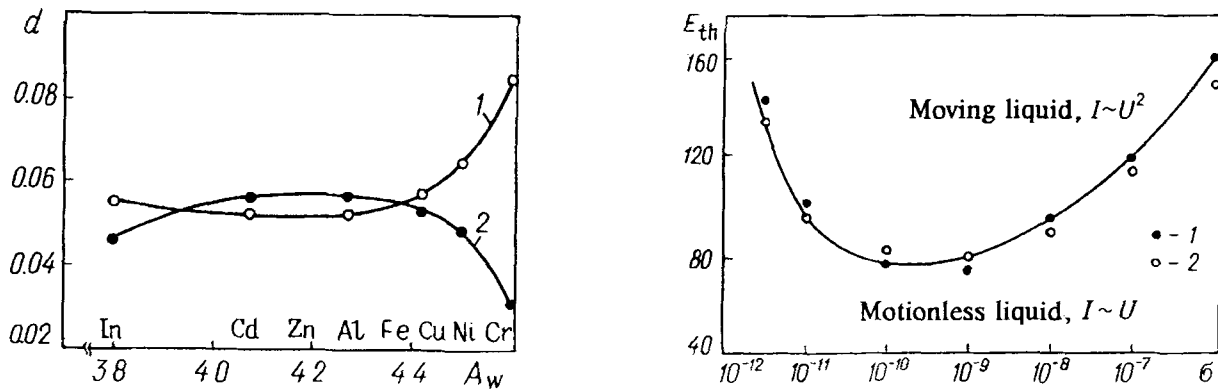


Fig. 4. Thickness of near-electrode layers versus electrode material for the electronic work function in vacuum (the same material of the electrodes, 5% BA solution in TO,  $U = 1$  kV): 1, 2) see Fig. 3.

Fig. 5. Plot  $E_{th}$  versus  $\sigma$  for BA solutions in TO: 1) the origin of VAC nonlinearity; 2) the beginning of liquid self-motion.  $E_{th}$ , kV/m.

It has turned out that the near-electrode layer width established with time reaches its maximum at electric intensities corresponding to the regime of developed electric convection [5]. The latter "washes away" the space charge of the liquid formed near the electrode and prevents build-up of the layer. This correlates with the fact that near the electrode, where convection initiates, the near-electrode layer is always larger, i.e., for the low-voltage conductivity of the liquid,  $10^{-12}$ – $10^{-11}$   $\Omega^{-1} \cdot m^{-1}$  (Fig. 3b), convection starts mainly from the anode, for  $10^{-10}$ – $10^{-9}$   $\Omega^{-1} \cdot m^{-1}$  predominantly from the cathode, and for  $10^{-9}$ – $10^{-8}$   $\Omega^{-1} \cdot m^{-1}$  from both electrodes.

The extremal character of the curve in Fig. 3b is explained by the fact that the number of clusters increases upon initial addition of the admixture (BA) to the main liquid (TO) and, as a consequence, the layer thickness and the convection intensity increase up to some level. On further adding of the admixture, the intensity is observed to decrease because of decreasing cluster size and recombination. The change of polarity in this case is attributable to the different character of charge carriers in the main liquid medium and in the admixture.

Since the processes of electrochemical charge injection on the electrodes depend on the electronic work function of the electrode metal, this has also affected the thickness of the near-electrode layer (Fig. 4). The layer thickness near the anode remains practically unchanged, while at the cathode an extremum near 4.2–4.4 eV is observed which correlates with the results obtained by the pulsed VAC method and has the same explanation.

After cessation of the transition processes a steady regime of ion-cluster conduction sets up in the liquid, which has been investigated at d.c. current. The appropriate measurements have shown that Ohm's law is also obeyed in this case; it is violated only when a certain value of electric intensity ( $E_{cr}$ ) is exceeded, after which the liquid passes into the state of self-motion and the current in it becomes proportional to the squared voltage across the electrodes. The critical electric intensities at which Ohm's law is violated and the liquid starts self-motion

(coincidence with an accuracy of up to 5%) depend on the low-voltage conductivity of the liquid; the corresponding dependence is shown in Fig. 3b. At low concentrations of charge clusters or their recombination stronger fields are required for convection initiation in the liquid. The above results point to a complicated composition of the near-electrode layer in the case of charge injection from the electrode surface and from the corresponding ionic layer near them. Here, consideration should be also given to its particular form realized by locally ordered molecular structures like the injection of charged drops from a freely charged liquid surface.

## NOTATION

$A_w$ , electronic work function of electrode material in vacuum;  $I_{sur}$ , electric current across electrode surface;  $U_{sur}$ , voltage applied to adsorbed liquid layer;  $U_{th}$ , threshold  $U_{sur}$  value at which Ohm's law is violated;  $E_{d.l.}$ , electric intensity in electric double layer;  $d$ , thickness of adsorbed near-electrode layers;  $\sigma$ , low-voltage conductivity of liquid;  $E_{cr}$ , critical mean electric intensity in the liquid at which its convection begins.

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