

CONTACT PHENOMENA IN POORLY CONDUCTING LIQUID MEDIA

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A model of the ion-cluster mechanism of contact phenomena in poorly conducting liquid media is presented. An analytical description of this phenomenon is carried out.

General Model. The conclusion that poorly conducting liquids (depending on the method of their preparation) comprise a mixture of nonpolar organic compounds with a dissociating polar admixture (with an equilibrium dissociation constant of about 10^{-8}) can be drawn based on results of numerous experiments. Ions formed during the dissociation of admixture molecules participate in electrochemical reactions on electrodes, and neutral reaction products leave the electrodes due to diffusion, migration, and convective transfer and recombine inside the liquid. Charge transfer due to electron capture by neutral molecules of the liquid is also possible, but its efficiency is lower.

Taking into account the multivariant and multistage character of electrochemical reactions in organic liquids [1], it is reasonable to restrict oneself, when describing contact phenomena, to a general consideration of the following reactions of ionization of a neutral substance (cathode and anode, respectively)



and two reactions of neutralization of the ions formed (cathode and anode, respectively):



where k_1, k_3, k_5, k_7 are the rates of forward and k_2, k_4, k_6, k_8 are the rates of reverse reactions on the electrodes. The function of ion triplets can be neglected, since they do not contribute substantially to conductivity. Thus, we consider the dissociation injection mechanism of the conductivity of the medium when charge carriers emerge and disappear on both of the electrodes.

The interaction of ions with deformed external shells of polar and polarized molecules of the liquid is an important feature of this mechanism. A simple calculation shows that at observed dissociation degrees of electrolytic admixtures each ion in the electric field transports a molecular complex of $10^7 - 10^8$ neutral molecules of the liquid (this stems from the sole fact of the existence of electric convection in poorly conducting liquids). The existence of complexes of the type which are formed due to hydrogen bonding of polar and polarized molecules of the liquid to each other (charge clusters) has been proved experimentally and explained on the model level in [2, 3].

Charge clusters form ordered molecular structures on the surface of electrodes which have preferentially ionic conductivity realized by means of electrochemical charge injection following reactions (1) and (2). In this case a specific kind of the charge injection similar to the injection of charged droplets with a free charged surface of the liquid is realized on the boundary of these structures (at distances of about 10^{-5} to 10^{-4} m from electrode surfaces). The analytical description of this conductivity mechanism is reduced to investigation of basic equations of electrohydrodynamics [4] with regard for the kinetics of electrochemical reactions on electrodes and specific regularities of the transfer coefficients characteristic of charge clusters. In general form the system of equations is rather complex:

$$\mathbf{J}_1 = b_1 \rho_1 \mathbf{E} - D_1 \nabla \rho_1 + \rho_1 \mathbf{v}, \quad (3)$$

$$\partial \rho_i / \partial t + \operatorname{div} \mathbf{J}_i = g_i, \quad (4)$$

$$\sum_i \rho_i = \varepsilon \varepsilon_0 \operatorname{div} \mathbf{E}, \quad (5)$$

$$\partial \mathbf{v} / \partial t + (\mathbf{v}, \nabla) \mathbf{v} = \nu \nabla^2 \mathbf{v} - (1/\gamma) \left\{ \nabla P + \left(\sum_i \rho_i \right) \mathbf{E} \right\}, \quad (6)$$

$$\operatorname{div} \mathbf{v} = 0. \quad (7)$$

In the present work, system (3)-(7) is applied to the case of stationary electric current through a binary electrolyte in a cell with infinite plane-parallel electrodes in the undeveloped convection mode. In this case, in the absence of induced dissociation and recombination of ions in the liquid it takes the following form:

$$j_1 = b_1 \rho_1 E - D_1 \rho_1', \quad (8)$$

$$j_2 = b_2 \rho_2 E - D_2 \rho_2', \quad (9)$$

$$\rho_1 + \rho_2 = \varepsilon \varepsilon_0 E', \quad (10)$$

$$j_1' + j_2' = 0, \quad (11)$$

where the prime stands for the first derivative with respect to the coordinate x directed along the field normally to the electrodes.

Boundary Conditions for System (8)-(11). When setting up boundary conditions, one should use the circumstance that disruptions of the electrically neutral character of poorly conducting liquids decrease rather rapidly with distance from the electrodes. This makes it possible to seek solutions of equations (8)-(11) in the class of functions

$$E'(x), \rho_1'(x), \rho_2'(x) \xrightarrow{x \rightarrow \infty} 0 \quad (12)$$

and define the constants j_1 and j_2 as

$$j_1 = b_1 \rho_1^0 E_0, \quad j_2 = b_2 \rho_2^0 E_0, \quad (13)$$

where ρ_1^0, ρ_2^0 , and E_0 are the partial charge densities and the strength of the electric field at a sufficient distance from the electrodes. Constraint (12) is formulated in the form of two boundary conditions for system (8)-(11):

$$E(x)|_{x \rightarrow d/2} = E_0(1 + \Delta), \quad |\Delta| \ll 1, \quad (14)$$

$$E'(x)|_{x \rightarrow d/2} = \frac{E_0}{r_D}, \quad (15)$$

where d is the distance between the electrodes and r_D is the average Debye radius in the liquid.

The third condition stems from a consideration of the kinetics of electrochemical reactions on electrodes. Namely, the following expression holds [6] for the density of the electrochemical injection current on the electrode (e.g., cathode) surface in the course of reaction (1):

$$j_1 = -k_1^0 N e \left[\exp \left(-\frac{\alpha e \Delta \varphi_1}{kT} \right) - \exp \left(\frac{\beta e \Delta \varphi_1}{kT} \right) \right], \quad (16)$$

where N is the volume density of neutral particles X in the vicinity of the electrode surface, e is the positron charge, α is the transfer coefficient, $\beta = 1 - \alpha$, $\Delta \varphi_1$ is the difference of potentials of the electrode surface and particle X , k_1^0 is the rate constant of reactions (1), which is related to k_1 and k_2 as

$$k_1^0 = k_1 \exp \left(-\frac{\alpha e \varphi_1^0}{kT} \right) = k_2 \exp \left(\frac{\beta e \varphi_1^0}{kT} \right), \quad (17)$$

where φ_1^0 is the equilibrium potential of the electrode corresponding to a zero value of j_1 . Inasmuch as poorly conducting liquids can include low-concentration electrolyte solutions (their dissociation degree $\alpha_d \sim 10^{-8}$), according to [5]

$$\alpha = \beta = 1/2 \quad (18)$$

and the following expression for j_1 holds:

$$j_1 = 2k_1^0 N e \sinh \left(\frac{e \Delta \varphi_1}{2kT} \right). \quad (19)$$

Then, taking into account that

$$\rho_1^0 = -\alpha_d N e, \quad b_1 = -|b_1|, \quad \Delta \varphi_1 \approx \lambda_1 E_1, \quad (20)$$

where $E_1 = E_1(x)|_{x \rightarrow d}$ is the strength of the electric field in the vicinity of the electrode (in the particular case, the cathode), and λ_1 is the width of the ionization layer, which is comparable with the particle size X , we arrive at

$$E_1(x)|_{x \rightarrow d} = \frac{2kT}{\lambda_1 e} \operatorname{arsinh} \left(\frac{\alpha_d |b_1| E_0}{2k_1^0} \right). \quad (21)$$

Condition (21) is taken as the third boundary condition of system (8)-(11). Conditions (14), (15), and (21) make it possible to determine the strength of the electric field $E_1(x)$ (with the accuracy of E_0) in the vicinity of the cathode. The similar formulation (14), (15) along with the condition

$$E_2(x)|_{x \rightarrow 0} = \frac{2kT}{\lambda_2 e} \operatorname{arsinh} \left(\frac{\alpha_d |b_2| E_0}{2k_2^0} \right) \quad (22)$$

makes it possible to determine the strength of the electric field in the vicinity of the anode ($E_2(x)$). An approximate solution for the entire interelectrode gap $E(x)$ is determined as a superposition of the two particular solutions

$$E(x) = E_1(x) + E_2(x) - E_0, \quad (23)$$

$$\int_0^d E(x) dx = \Delta \varphi, \quad (24)$$

where $\Delta \varphi$ is the potential difference of the electrodes.

In this formulation, the problem of evaluation of $E(x)$ is closed and is explored in what follows after refining the transfer characteristics of charge clusters.

Transfer Characteristics of Charge Clusters in Electric Field (Diffusion Coefficient D and Mobility Coefficient b). They can differ from the corresponding characteristics of free ions, which affects in a natural manner the coefficients of system (8)-(11). Mainly, these distinctions involve the D to b ratio

$$\varphi_* = Z \frac{D}{b}, \quad (25)$$

where Z is the charge number of the cluster.

By considering the equilibrium state of a diffuse layer of clusters, one can write

$$\mathbf{j} = Zebn \mathbf{E} - ZDe\nabla n, \quad (26)$$

where \mathbf{j} is the density of the current of the selected kind of clusters and n is their concentration. (The polarization component of the current is not taken into account here, since the dipole moment equals zero for a spherically symmetric cluster.)

Inasmuch as the equation

$$n = n_0 \exp\left(-\frac{U}{kT}\right), \quad (27)$$

holds in the equilibrium state, with n_0 being the equilibrium concentration and U being the potential energy of clusters, then for the one-dimensional case (although this is not of the principal importance) we obtain

$$bn_0 E \exp\left[-\frac{U}{kT}\right] = -\frac{Dn_0}{kT} U' \exp\left[-\frac{U}{kT}\right]. \quad (28)$$

Taking into account that

$$U = Ze\varphi + W, \quad (29)$$

where φ is the potential of the electric field and W is the energy of the interaction of a cluster with its dipolar shell, we arrive at

$$\frac{D}{b} = \frac{ZkT}{\left(Ze - \frac{W'}{E}\right)} = \varphi_*. \quad (30)$$

Relationship (30) shows that for charge clusters in poorly conducting liquids, the value of φ_* depends on the composition of the liquid and voltage at the electrodes and can differ from the value of kT/e assumed in the electrochemistry of aqueous solutions.

In the general case, the D/b ratio can also be a function of the potential in the vicinity of the electrode surface. Indeed, by taking into account the Einstein correction [6] for the viscosity of diluted suspensions of spherical particles

$$\eta = \eta_0 \left(1 + \frac{10\pi}{3} nR^3\right), \quad (31)$$

where η and η_0 are the dynamic viscosities of the suspension and the host liquid, n and R are the concentration and radius of the particles (clusters), relationship (27) and the Stokes formula

$$b = \frac{1}{6\pi\eta R}, \quad (32)$$

we obtain

$$\frac{D}{b} = \frac{ZkT}{\left(Ze - \frac{W'}{E}\right)} \left[1 + \frac{10\pi}{3} R^3 n_0 \exp\left(-\frac{U}{kT}\right)\right]. \quad (33)$$

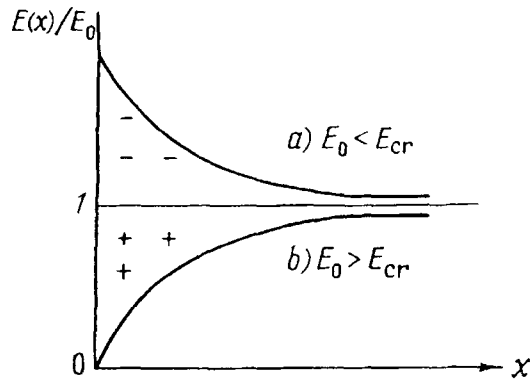


Fig. 1. Distribution of electric field in vicinity of electrode (anode) at various values of E_0 and constant D and b .

In the first stage, we will consider the coefficients D and b as being constant and varying their ratio φ_* depending on the type of liquid and the voltage on the electrodes. In what follows, we will also take into account dependence (33).

For constant D and b , system (8)-(11) can be reduced [7] to the following resultant equation:

$$\frac{d^2 f}{d\xi^2} = af^3 + (1-a)f - 1, \quad (34)$$

$$f = \frac{E}{E_0}, \quad \xi = \frac{x}{r}, \quad a = \frac{r^2 E_0}{2\varphi_*^2}, \quad r = \frac{\varepsilon \varepsilon_0 \varphi_*}{2\alpha_d ZNe}. \quad (35)$$

We investigated Eq. (34) earlier [7], and managed to find its exact particular solution realized under conditions (14)-(15):

$$f = 1 \pm \frac{2(2a+1)}{\sqrt{2a} \sinh[\sqrt{2a+1}(\xi \pm C)] \pm 2a}, \quad (36)$$

where

$$C = \frac{1}{\sqrt{2a+1}} \operatorname{arsinh} \frac{2(af(0) + a + 1)}{\sqrt{2a}(f(0) - 1)}. \quad (37)$$

Uniqueness of solution (36) is achieved by choosing the plus sign when $f(0) > 1$ and the minus sign when $f(0) < 1$. At $f(0) = 1$ we choose $f(\xi) \equiv 1$. The variant $f(0) > 1$ is realized when $E_0 < E_{cr}$. In this case a heterocharge region is formed in the vicinity of the electrode (Fig. 1a). The variant $f(0) < 1$ is realized when $t_0 > t_{cr}$. In this case a homocharge region is formed in the vicinity of the electrode (Fig. 1b). At $f(0) = 1$, $E_0 = E_{cr}$ and the fluid is electrically neutral. The quantity E_{cr} is determined from the equation

$$E_{cr} = \frac{2kT}{\lambda_1 e} \operatorname{arsinh} \left(\frac{\alpha_d |b_1| E_{cr}}{2k_1^0} \right). \quad (38)$$

The solution found describes well the structures of homo- and heterocharge in near-electrode regions in poorly conducting liquids and makes it possible to determine the value of φ_* by comparison of the theoretical and experimental curves. As has been assumed, this procedure revealed that φ_* is determined by the composition of the poorly conducting liquid and depends on the voltage on the electrodes. Corresponding dependences for solutions of butyl alcohol in transformer oil are presented in Fig. 2.

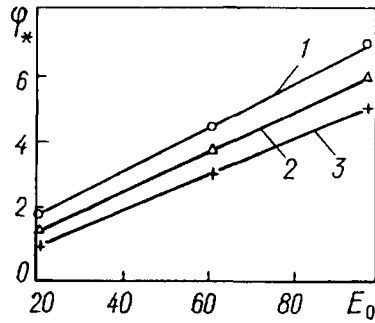


Fig. 2. Dependence of characteristic potential φ_* on strength of electric field E_0 : 1) $\sigma = 10^{-9} \text{ Ohm}^{-1}/\text{m}^{-1}$; 2) 10^{-10} ; 3) 10^{-11} . E_0 , kV/m; φ , V.

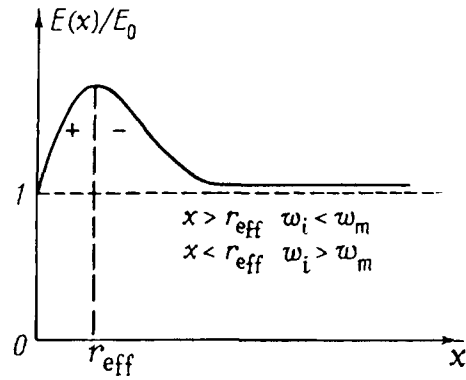


Fig. 3. Distribution of strength of electric field in vicinity of electrode (anode) for various D and b .

In addition to homo- and heterocharge structures, more complex bipolar structures have been found in experiments [8]. These structures can be described only by means of a numerical investigation of system of equations (8)-(11) with regard for relationship (33). Calculations have shown that in this case a satisfactory coincidence of the theory and experiment can be achieved at the same values of φ_* as in the case of monotonic distributions (36) and (37). The emergence of an extremum of the strength of the electric field is explained by the fact that a change in the mobility of clusters in the surface layer with the thickness

$$r_{\text{eff}} \sim \frac{r}{\sqrt{2a + 1}} \quad (39)$$

leads to a change in the balance of rates of ionization of the neutral substance and migration of cluster ions. As a result, the sign of the space charge changes in the vicinity of the electrode surface ($x < r_{\text{eff}}$), the entire near-electrode layer of the liquid appears to be bipolar-charged, and is described by a distribution of the strength of the electric field with an extremum at the point r_{eff} (Fig. 3).

The quantity E_{cr} , defined as a root of equation (38), corresponds to the onset (with respect to the voltage) of an unstable distribution of the space charge with Coulomb forces directed from the electrode to the liquid. When E_{cr} is surpassed, the emergence of electric convection should be expected in the liquid. In the experiments with butyl alcohol in transformer oil, the phenomenon is observed at average strengths of the electric field exceeding 500–1000 V/cm. Calculation of the root of (38) at $\alpha_d \sim 10^{-8}$, $\lambda \sim 5 \cdot 10^{-10}$ m, $b \sim 5 \cdot 10^{-7} \text{ m}^2/(\text{V} \cdot \text{sec})$, $T = 300$ K, and $k_1^0 \sim 10^{-15}$ m/sec (5% solution) yields the value $E_{\text{cr}} \approx 400$ V/cm, which is pretty close to the experimentally observed value of 500 V/cm. The coincidences with the experiment enumerated count in favor of the model of the ion-cluster conductivity chosen and make it possible to formulate results of its investigation in the following manner:

1. The region of low electric-field strengths $E_0 < E_{\text{cr}}$ ($\sim 5 \cdot 10^3$ V/m). Here the density of the electric current in poorly conducting liquids is mainly determined by its migration component $(b_1\rho_1 + b_2\rho_2)E$. This is connected with the fact that the migration velocity of charge carriers (w_m) in the liquid

$$w_m = \alpha_d N b_{1,2} E \quad (40)$$

is linear with the strength of the electric field and, according to (38), exceeds the rate of their formation (ionization) on the electrodes (w_i)

$$w_i = k_{1,2}^0 N \sinh \left(\frac{e\lambda_{1,2} E}{2kT} \right). \quad (41)$$

An excess heterocharge is formed in near-electrode layers, the liquid is immobilized, and its volt-ampere characteristic is linear. Deviations from Ohm's law can appear here only at very low strengths of the electric field (~ 1

V/m), when the potential of the electrodes approaches its equilibrium value and the electrochemical injection current decreases sharply (exponentially) to zero (5).

2. *The region of moderate (prebreakdown) electric-field strengths* $E_{cr} \leq E_0 < E_{break}$ ($\sim 5 \cdot 10^3 - 5 \cdot 10^5$ V/m). Here the rate of the formation of ions on the electrode surface exceeds their migration rate in the liquid, and an excess homocharge is formed in the near-electrode layer, which leads to electric convection. As a result, a convective component of the electric current density (ρv) appears, which begins to prevail with increasing voltage on the electrodes. Inasmuch as the distribution of the strength of the electric field in the interelectrode gap $E(x)$ has, according to Eq. (36), an exponential character, then

$$\rho(x) \sim E'(x) \sim E(x). \quad (42)$$

This, according to dimensional analysis of Eq. (6), yields

$$v \sim E, \quad (43)$$

from which it follows that the volt-ampere characteristic of the liquid acquires the quadratic dependence on the voltage:

$$j = j_1 + j_2 \sim \sigma_1 E + \sigma_2 E^2. \quad (44)$$

3. *The region of high (breakdown) electric-field strengths* $E_0 \geq E_{break}$ ($\sim 5 \cdot 10^5$ V/m). The differences in the rates of formation of ions on the electrodes and their transfer to the liquid become so large that neither migration nor the convective components of the density of the electric current in the liquid can compensate for the disbalance formed. This leads to the emergence of instabilities of various kinds (thermal, hydromechanic, etc.) in the near-electrode region, which then transform into streamer branches of electric breakdown in the liquid [4]. The volt-ampere characteristic becomes exponential.

NOTATION

γ , ν , and $\epsilon\epsilon_0$, volume density, kinematic viscosity, and dielectric permeability of liquid; P , pressure; J_i , ρ_i , b_i , and D_i , partial densities of currents and space charges and mobility and diffusion coefficients of ions of the i -th kind; g_i , source function for the i -th kind of ions; E and v , strength of electric field and mechanical velocity of flow of liquid; k , the Boltzmann constant; T , absolute temperature; E_{cr} , critical value of strength of electric field beyond which the liquid is electroneutral near electrode; r_{eff} , distance from electrode surface at which equality of the rate of ionization of the neutral substance on the electrode and the migration rate of charge carriers in liquid takes place due to a change in the mobility of the clusters.

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