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Relaxation and Two-dimensional Phase Transitions in the Electrical Double Layer

V.A.Benderskii and G.I.Velichko

The excess entropy of formation and the characteristic relaxation times of the electrical double layer at the interface between the metal and electrolyte solution have been determined by the laser temperature jump method, consisting in the measurements of the electrical signal of an electrochemical cell on heating a metallic electrode by nanosecond laser pulses. The combination of the laser temperature jump data and data obtained by electrochemical methods shows that the orientational rearrangement of the solvent monolayer and the adsorption of surfactants occurring when the electrode potential and the solution composition are altered have the character of two-dimensional first- and second-order phase transitions.
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I. INTRODUCTION

Data obtained by classical electrochemical surface tension and differential capacitance methods serve as the experimental basis for the electrochemical double layer (EDL) theory. Their measurement at the interfaces beween electrolyte solutions and ideally polarisable metallic electrodes with atomically smooth surfaces, in particular, the mercury electrode, has ensured a quantitative descriptiion of the principal phenomena: the formation of surface excess amounts of ions in the dense and diffuse parts of the EDL and the adsorption in its inner part of dipolar solvent molecules, ions, and surfactants (see, for example, Frumkin[1] and Delahay[2]). However, in connection with the development of theoretical models of the EDL, for the testing of which it is necessary to have data on its structure and dynamic properties, it was discovered that these traditional methods have limitations. The study of the packing and orientation of the molecules and of the interactions between them, of the molecular mobility in the interface, of the change in the degree of hydration of the ions on passing from the bulk of the solution to the EDL, and of a multiplicity of similar questions stimulated the creation of new

methods. One of these is the method of the laser temperature jump (LTJ) in which the temperature coefficients of the decrease in the potential and the characteristic relaxation times of the EDL are measured. The first of these quantities is thermodynamic and in this respect the LTJ method supplements the traditional electrochemical methods. The dependences of the relaxation times on the electrode potential and the solution composition, first measured with the aid of the LTJ method, revealed a relation between the dynamics of the EDL and its structure.

The first studies of the EDL by this method were closely related to the investigation of photoemission from metals into electrolyte solutions.[3] In one of the first studies of the characteristics of the photoemission,[4] it was observed that the change in the potential of the electrode following its pulse illumination is caused not only by the emission of electrons from the metal into the solution but also by the heating of the electrode by the light absorbed in it. The pulse heating signal γ_h was separated from the photoemission signal using light at a sufficiently long wavelength for which there is no photoemission. According to Korshunov et al.,[4] γ_h exhibits a characteristic dependence on the electrode potential E and, in particular, it changes sign near the zero-change potential (ZCP). Barker and Cloke,[5] who studied the $\gamma_h(E)$ relation in greater detail, observed a shift of the zero response potential (ZRP), at which $\gamma_h = 0$, relative to the ZCP, amounting to between −0.10 to −0.15 V and being caused by the dipole potential jump. At the ZRP, the water dipoles in the inner part of the EDL undergo reorientation. Barker and Cloke[5] studied the $\gamma_h(E)$ relations in acid solutions and showed that γ_h has a constant component due to thermal diffusion.

In the first investigations,[4,5] the electrode was heated by light pulses with a duration $t_0 \gtrsim 10^6$ s, whereupon the kinetics of the heating signal are determined by the form of the pulse and the time constant of the electrochemical cell. Measurements have been made[6] of $\gamma_h(E, t)$ on laser heating ($t_0 \cong 10^{-8}$ s), which showed that in dilute electrolyte solutions in the vicinity of the ZCP, the relaxation time of the diffuse part of the EDL corresponds to the time of the diffusional displacement of ions by the Debye length, while the relaxation time of the dense part of the EDL increases sharply over a wide range of potentials close to ZRP.

It has been shown[7] that the heating signal is proportional to the derivative of the excess entropy of the EDL S^σ with respect to the charge of the electrode, i.e. S^σ has an extremum at the ZRP. In the range of potentials corresponding to the ideal polarisability of the mercury electrode, three ZRP, corresponding to two maxima and a minimum in S^σ maxima, the sharp increase in the relaxation times in their vicinity, and also the anomalies in the excess heat capacity calculated from the temperature variations of S^σ justify the hypothesis that the orientational rearrangement of the monolayer of water dipoles in the inner part of the EDL, occurring under the influence of its electric field, is a two-dimensional second-order phase transitions.[8,9]

Further investigations by the LTJ method demonstrated that the $\gamma_h(E)$ and $\tau(E)$ relations are extremely sensitive to the change in the structure of the EDL associated with the adsorption of inorganic anions and surface-active organic substances.

The question of two-dimensional phase transitions was raised in one of the first communications by Frumkin,[10] who stated that, in the presence of a strong intermolecular attraction of the adsorbed organic molecules, the adsorption layer becomes a two-phase formation in a certain range of coverages. This interaction is taken into account phenomenologically in the Frumkin adsorption isotherm by the introduction of the attraction constant, at the critical value of which a first-order phase transition occurs.[11] Application of the LTJ method established that the cooperative rearrangement of the EDL takes place as a result of transitions of different orders.

In the present review the principles of the new method and the results of its application are consistently examined for the first time.

II. PULSE HEATING OF THE METALLIC ELECTRODE

The change in the temperature of the surface of a metal in contact with a solution under the influence of a light pulse absorbed by the metal is described by the relation (see, for example, Benderskii and co-workers):[3,7]

$$\Delta T(t) = \frac{L(1-R)}{\sqrt{\pi\kappa c\rho}}\left(1+\sqrt{\frac{\kappa_1 c_1 \rho_1}{\kappa c\rho}}\right)^{-1}\int_0^t \frac{f(t')}{\sqrt{t-t'}}\,dt' \,, \qquad (1)$$

where κ, c, ρ, κ_1, c_1, and ρ_1 are the thermal conductivities, heat capacities, and densities of the metal and solution respectively, L is the light intensity, R the coefficient of the reflection of light by the metal, and the normalised function $f(t)$ describes the form of the laser pulse. The maximum temperature jump generated by a pulse with a duration t_0 is

$$\Delta T_m = \frac{L(1-R)}{\sqrt{\pi\kappa c\rho}}\left(1+\sqrt{\frac{\kappa_1 c_1 \rho_1}{\kappa c\rho}}\right)^{-1}\sqrt{t_0} \,. \qquad (2)$$

The time variation of the surface temperature at $t \gg t_0$ is independent of the characteristics of the metal and is described by the relation

$$\Delta T(t) = \Delta T_m \sqrt{\frac{t_0}{t}} \,. \qquad (3)$$

Relations (1)–(3) are valid when the thickness of the electrode d and the size of the laser spot, i.e. the diameter of the heating zone r, satisfy the condition implying that the heat is removed solely along the normal to the interface and that there is no increase in the heated area:

$$d, r \gg 2\sqrt{\frac{\kappa}{c\rho}t} \,. \qquad (4)$$

For a liquid mercury electrode placed in an aqueous solution ($\kappa = 7.9 \times 10^{-2}$ J cm^{-1} K^{-1} s^{-1}, $c = 0.14$ J g^{-1} K^{-1}, $\rho = 13.6$ g cm^{-3}, $\kappa_1 = 5.9 \times 10^{-3}$ J cm^{-1} K^{-1} s^{-1}, $c_1 = 4.2$ J g^{-1} K^{-1}, and $\rho_1 = 1.0$ g cm^{-3}) and illuminated with light at a wavelength 500–700 nm ($R \cong 0.70$ for normal incidence), the quantity $\Delta T_m/L = 2.2 \times 10^{-5}$ K kW^{-1} cm^2 when $t_0 = 4$ ns. This estimate shows that heating of the electrode by 1–2 K is effected by a light pulse with a peak power of 50–100 kW cm^{-2}. For the working electrodes with an area of approximately 10^{-3} cm^2 usually employed in measurements, this heating can be readily achieved with the aid of the usual nanosecond lasers having a peak power of 1–10 kW.

For observation times ranging from 10^{-8} to 10^{-6} s, the thicknesses of the heated layers of the metal and solution are 10^{-5}–10^{-4} cm and 10^{-6}–10^{-5} cm respectively, which means that the temperature jumps are localised outside the EDL in the bulk of the metal solution, i.e. the LTJ signal arises in the following galvanic cell:

metallic electrode	heated zone in the metal	heated zone in the solution	solution

and has three components:

$$\gamma_h = \gamma_{h1} + \gamma_{h2} + \gamma_{h3} \qquad (5)$$

determined by the thermo-e.m.f. of the metal ($\mathscr{V}_{h3}$), the thermal diffusion potential of the solution ($\mathscr{V}_{h2}$), and the temperature coefficient of the decrease in the potential of the EDL $\mathscr{V}_{h1}$. The temperature jump induces a change in the potential of the EDL due to the temperature variation of its capacitance and composition. When the time constant of the electrochemical cell is large compared with the observation time, the outer source of polarisation does not have sufficient time to alter the initial charge of the electrode q, so that $\mathscr{V}_{h1}$ is recorded under coulombostatic conditions. The following relations are valid for low values of ΔT:

$$\mathscr{V}_{h1}=\left(\frac{\partial\varphi}{\partial T}\right)_q\Delta T,\ \mathscr{V}_{h2}=\alpha\Delta T,\ \mathscr{V}_{h3}=\alpha_s\Delta T \tag{6}$$

where $(\partial\phi/\partial T)_q$ is the temperature coefficient of the decrease in the potential in the EDL. When $q = 0$, this quantity is known for a series of electrochemical systems[12,13] and is of the order of magnitude of 10^{-3} VK^{-1}, which exceeds by two orders of magnitude the coefficients of the thermo-e.m.f. α of metals, i.e. $\mathscr{V}_{h1}\gg\mathscr{V}_{h2}$. The coefficient α_s is given by [14]

$$\alpha_s=\sum_i\frac{t_i}{z_i}S_i \tag{7}$$

where S_i is the transport entropy of ions of the ith kind having a charge z_i and a transport number t_i. The values of α_s for ions without anomalous mobility are of the order of 10^{-5} VBK^{-1}, so that the contribution of thermal diffusion to the LTJ signal can also be neglected. For solutions containing the anomalously mobile hydrogen and hydroxide ions, this contribution is significant and adds to $\mathscr{V}_h$ a component which is independent of the electrode potential.[7] With this exception, the LTJ signal is determined with adequate accuracy by the characteristics of the EDL and not the bulk phases:

$$\mathscr{V}_h\simeq\left(\frac{\partial\varphi}{\partial T}\right)_q\Delta T\ . \tag{8}$$

III. TEMPERATURE COEFFICIENTS OF THE POTENTIAL DROP IN THE ELECTRICAL DOUBLE LAYER

For a constant potential and phase composition, the equation of the electrocapillary curve is

$$-\mathrm{d}\gamma=\Gamma_s\mathrm{d}T+q\mathrm{d}E_\pm+\Gamma_\mp\mathrm{d}\mu\ , \tag{9}$$

where γ is the surface tension, $\Gamma_\pm$ the relative excess surface amounts of cations and anions respectively, $E_\pm$ the potential of the electrode, measured relative to the reference electrode, reversible with respect to the cations or anions, and Γ_S the excess surface entropy defined by the relation

$$\Gamma_S=S_{int}-m_M^\sigma S_M^0-m_W^\sigma\left(S_W^0-\frac{n_S}{n_W}S_S^0\right) \tag{10}$$

where S_{int} is the specific surface entropy, m_M^σ and m_W^σ are the numbers of moles of the metal and water per unit surface area, n_W and n_S the volume fractions of water and the salt, and S_M^0, S_W^0, and S_S^0 the standard entropies of the metal, water and the salt. Instead of Γ_S, we shall introduce the excess entropy of formation of the EDL, which is equal to the difference between the entropies of the components at the interface and in the bulk phases:

$$S^\sigma=S_{int}-m_M^\sigma S_M^0-m_W^\sigma S_W^0-m_+^\sigma S_+-m_-^\sigma S_-\ , \tag{11}$$

where S_+ and S_- are the entropies of the ions at the given activity of the salt. Bearing in mind that the electrode charage is equal to the difference between the excess surface amounts of the ions, we find from Eqns.(10) and (11)

$$q=\Gamma_--\Gamma_+ \tag{12}$$

$$\Gamma_s=S^\sigma+\Gamma_\pm S_s\mp qS_\mp \tag{13}$$

For a 1 : 1 electrolyte, the relation between the potential measured relative to the reference electrode and the potential drop in the EDL is described by the expression

$$F\,\mathrm{d}E_\pm=F\,\mathrm{d}\varphi\mp S_-\,\mathrm{d}T\pm\frac{1}{2}RT\,\mathrm{d}\ln a\ , \tag{14}$$

where F is the Faraday. In Eqn.(14), account was taken of the fact that

$$\mathrm{d}\mu=-S_s\mathrm{d}T+RT\mathrm{d}\ln a;\ S_s=S_s^0-R\ln a,\ \frac{\mathrm{d}\mu_\pm}{\mathrm{d}\ln a}=\frac{1}{2}RT,$$

where a is the activity of the salt. On substituting Eqns.(12)–(14) in Eqn.(9), we find

$$-\mathrm{d}\gamma=q\,\mathrm{d}\varphi+RT\left(\Gamma_\pm\pm\frac{q}{2F}\right)\mathrm{d}\ln a+S^\sigma\,\mathrm{d}T \tag{15}$$

Under coulombostatic conditions, used in the LTJ measurements, the thermodynamic potential is represented by the function

$$\xi=\gamma+q\varphi\ , \tag{16}$$

and, on going over to the latter, we obtain the main relation

$$-\mathrm{d}\xi=-\varphi\,\mathrm{d}q+RT\left(\Gamma_\pm\pm\frac{q}{2F}\right)\mathrm{d}\ln a+S^\sigma\,\mathrm{d}T. \tag{17}$$

The cross differentiation of Eqn.(17) leads to the relations

$$-\left(\frac{\partial\varphi}{\partial T}\right)_{a,q}=\left(\frac{\partial S^\sigma}{\partial q}\right)_{a,T}\ , \tag{18}$$

$$\left(\frac{\partial S^\sigma}{\partial\ln a}\right)_{q,T}=R\left(\Gamma_\pm\pm\frac{q}{2F}\right)+RT\left(\frac{\partial\Gamma_\pm}{\partial T}\right)_{a,q}\ . \tag{19}$$

The first of these relations constitutes the basis of the LTJ method and follows directly from the expression for the free energy of the charged interface:

$$\Delta G^\sigma=\Delta Q_0^\sigma+\int_0^q\varphi(q)\,\mathrm{d}q\ , \tag{20}$$

where ΔG_0^σ describes the non-electrical component of the free energy related, in particular, to the chemisorption and interaction of the adsorbed species with one another. Eqn.(19) relates the derivative of S^σ with respect to the activity of the salt to the temperature coefficient of the surface excess amounts. Under coulombostatic conditions, the first part of Eqn.(19) is the same for the anions and cations by virtue of relation (12). Differentiation of Eqn.(19) with respect to q yields the dependence of $V_h=(\mathscr{V}_h/\Delta T)=(\partial\varphi/\partial T)_{a,q}$ on the salt concentration:

$$\left(\frac{\partial V_h}{\partial\ln a}\right)_q=-R\left[\left(\frac{\partial\Gamma_\pm}{\partial q}\right)_{a,T}\pm\frac{1}{2F}\right]-RT\left(\frac{\partial^2\Gamma_\pm}{\partial q\,\partial T}\right)_a. \tag{21}$$

It follows from Eqn.(18) that, by measuring the dependence of V_h on q by the LTJ method, it is possible to find $S^\sigma(q)$ to within a constant, which is independent of q:

$$S^\sigma(q)=S^\sigma(0)+\int_0^qV_h(q)\,\mathrm{d}q\ . \tag{22}$$

Eqn.(21) relates the concentration variation of V_h to the surface excess amounts of the ions and their temperature coefficients.

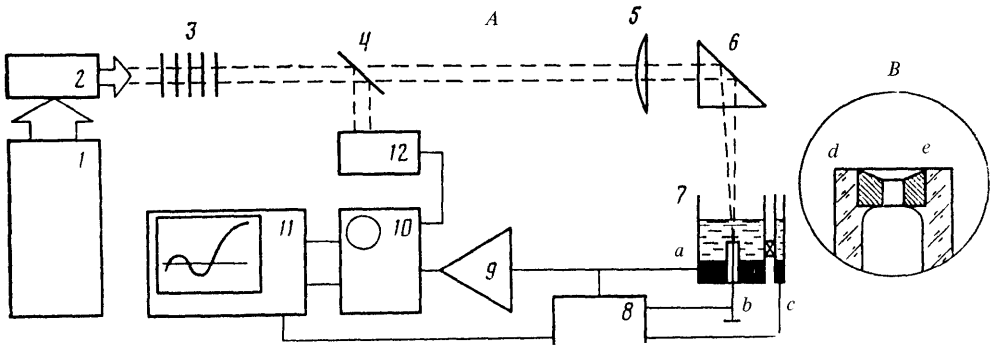


Figure 1. Circuit of the laser electrochemical relaxometer: 1) nitrogen laser used to pump the dye-based laser; 2) and 3) set of calibrated light attenuators; 4) semitransparent plate; 5) focussing lens; 6) rotatable prism; 7) electrochemical cell [*a*) measuring electrode; *b*) polarising electrode; *c*) reference electrode]; 8) polarisation and electrode potential scanning circuit; 9) amplifier of the LTJ signal; 10) stroboscopic oscillograph; 11) two-coordinate pen recorder; 12) circuit for the recording of laser pulses and the synchronisation of the strobe illumination (*A*); *B*) design of the working electrode in the electrochemical cell 7 [*d*) glass capillary; *e*) platinum ring].[7]

IV. METHODS OF MEASUREMENT

The LTJ method has been described in detail.[7] The circuit of the laser electrochemical relaxometer, designed for LTJ measurements, is illustrated in Fig.1. Heating is achieved by means of pulses from a laser based on rhodamine 6G (λ = 595 nm). At the selected light wavelength, the influence of photoemission can be neglected at electrode potentials more positive than −1.5 V.† The duration of the laser pulse is 4 ns for a peak power of 3 kW. The form of the pulse is recorded by a high-speed photocell. The laser light is focussed onto the cathode of the electrochemical cell. The LTJ signal is amplified by a broad band amplifier with a transmission band of approximately 200 mHz and is recorded by means of a stroboscopic oscillograph. When the frequency of the repetition of the laser pulses is 25 Hz, the stroboscopic conditions in the recording of the LTJ signal ensure its averaging over approximately 10^3 pulses, which makes it possible to achieve a sensitivity of the apparatus of 4×10^{-5} V, corresponding to minimum measurable values of V_h of 2×10^{-5} V K^{-1}. Further increase of sensitivity has been achieved[15] by employing a multichannel analyser in which the LTJ signal is divided by the amplitude of the laser pulse, which diminishes the error associated with the scatter of its values. Since the values of $(\partial\varphi/\partial T)_{q=0}$ for a series of solutions are known from independent electrochemical measurements,[10,11] the apparatus is calibrated directly in units of V_h and not γ_h, which eliminates the error associated with the determination of ΔT.

The working mercury electrode of the electrochemical cell (Fig.1) is made in the form of a smooth surface produced at the top of a glass capillary into which a thin platinum ring 0.35 mm in diameter has been sealed. As a result of the wetting of the ring with mercury, it is possible to avoid the appearance of capillary waves,[16] which interfere with the measurements, up to values of L = 1 MW cm^{-2}.

The $V_h(E)$ dependences are measured at a fixed instant. The delay of the instant of measurement relative to the maximum in the laser pulse is set at between 10 and 250 ns. The automatic scanning of the potential is performed after 30 − 100 s and the electrode surface is renewed after recording each $V_h(E)$ curve. The time variations of V_h are measured at constant electrode potentials. The relaxation time τ is determined by comparing the $V_h(t)$ kinetic curves with the curves calculated by Eqn.(1) for the measured form of the laser pulses. The relative values of τ for different E can be found to within 2 − 3 ns. The absolute values of τ contain a constant component which is determined by the transient characteristics of the cell and the amplifier. According to Benderskii and Velichko,[7] this component can be reduced to 5 − 10 ns. Konovalov and Raitsimring[15] succeeded in reducing its contribution to 1 − 2 ns.

In principle, the values τ may be found from the measured frequency dispersion of the differential capacitance. However, the scope of the high-frequency measurements is restricted by the time constant of the electrochemical cell, determined by the finite resistance of the volume of the electrolyte.[13,17] The maximum frequency of the measurements, attained at the present time, is 2 MHz and does not permit the observation of the relaxation of the EDL in the absence of the specific adsorption of organic substances.[17] The LTJ method is the only one which permits measurements of τ shorter than 10^{-6} S.

Eqn.(8) established a relation between V_h and the temperature coefficients of the differential capacitance of the EDL:

$$V_h = \left(\frac{\partial\varphi}{\partial T}\right)_{q=0} + \int_0^q \frac{\partial}{\partial T}\left(\frac{1}{C}\right) \mathrm{d}q \ . \qquad (23)$$

$$\frac{\partial V_h}{\partial q} = \frac{\partial}{\partial T}\left(\frac{1}{C}\right) \ . \qquad (24)$$

The validity of these relations in aqueous 0.5 M NaF solutions, for which the values of $\partial/\partial T(1/C)$ are known,[18,19] has been confirmed.[7] The $V_h(E)$ relations, measured by the LTJ method in aqueous 0.5 M NaF solution, agree with the relations calculated from the electrochemical data available for this solution,[18,19] which constitutes a test of the method. It must be emphasised that the accuracy of the determination of $V_h(E)$ from the temperature coefficients of the differential capacitance of the EDL is much lower than in the LTJ method. Despite the high accuracy of the measurement of C, reaching values to within 0.1 and 0.2% (see, for example, Charles et al.[20]),

† The potentials are read relative to the potential of the saturated calomel electrode.

the error in the measurements of $\partial C/\partial T$ is 5–10% owing to the smallness of the changes in C with temperature (0.01–0.10 F K^{-1}); integration with respect to E of the variable-sign function $\partial C/\partial T$, which enters into Eqn.(23), leads to errors in V_h up to 10–20%, increasing in the region of positive potentials under absorption conditions as a consequence of the increase in C. For this reason, there have been few calculations of the $S^{\sigma}(q)$ relations from electrochemical data.[20-23] Such measurements have been confined to the region of comparatively low positive charges ($q \leqslant 10$ μC cm^{-2}) and did not permit the discovery of a number of features of the EDL observed by the LTJ method.

V. THE LASER TEMPERATURE JUMP IN DILUTE ELECTROLYTE SOLUTIONS

According to the Gouy–Chapman theory, V_h is the sum of the temperature coefficients of the potential drop in the dense (φ^{M-2}) and diffuse (φ_2) parts of the EDL:

$$\left(\frac{\partial\varphi}{\partial T}\right)_q = \left(\frac{\partial\varphi^{M-2}}{\partial T}\right)_q + \left(\frac{\partial\varphi_2}{\partial T}\right)_q \qquad (25)$$

and the latter is given by

$$\left(\frac{\partial\varphi_2}{\partial T}\right)_q = \frac{\varphi_2}{T}\left(1 - \frac{kT}{e\varphi_2}\tanh\frac{e\varphi_2}{2kT}\right) . \qquad (26)$$

By measuring the dependence of V_h on q at different activities of the electrolyte and using Eqns.(25) and (26), two main postulates of the EDL theory have been tested:[7,24,25] the independence of the structure of the dense part of a, i.e. the constancy of $(\partial\varphi^{M-2}/\partial T)_q$ when a varies, and the validity of Eqn.(26), according to which the dependences of V_h on $(\partial\varphi_2/\partial T)_q$, calculated from Eqn.(26) for a different q should be represented by straight lines with identical slopes of unity. A similar method of testing the EDL theory has been used in the analysis of the differential capacitance curves.[2] The excess entropy of formation of the diffuse part of the EDL is

$$\Delta S_2 = -q\frac{\varphi_2}{T}\left(1 - \frac{3kT}{e\varphi_2}\tanh\frac{e\varphi_2}{4kT}\right) . \qquad (27)$$

If the theory is valid and ΔS^{M-2} is constant at different electrolyte activities, the relations between S^{σ} and ΔS_2 should be represented, as in the case of V_h, by straight lines with a slope of unity.

The $V_h(E)$ relations for the mercury electrode in aqueous NaF solutions with different electrolyte concentrations intersect at one point corresponding to the ZCP. As shown in Fig.2, the relations between V_h and $(\partial\varphi_2/\partial T)$ agree well with Eqns.(25) and (26) for $E \lesssim -0.1$ V. In the region of more positive potentials, the deviations exceed somewhat the insignificant adsorption of the fluoride ions. The excess entropy of formation of the EDL diminishes as the solution is diluted. The experimental relation between S^{σ} and ΔS_2 corresponds to the Eqn.(27).

Thus the results of the measurements agree well with the classical theory of the diffuse double layer in dilute electrolyte solutions (at concentrations below 0.1 M) in the absence of specific adsorption. Previously this theory was repeatedly confirmed by differential capacitance measurements (see, for example, Delahay[2]) and the LTJ method has made it possible to demonstrate that the thermal characteristics of the EDL are also described satisfactorily by it. It is noteworthy that the LTJ method not only yields an independent test of the theory of the concentration-dependent diffuse double layer but also makes it possible to find the values of φ_2 under conditions remote from the ZCP, where the influence the electrtolyte concentration on the CE curves is weakest and the accuracy of the determination of φ_2 by the differential capacitance method is reduced.

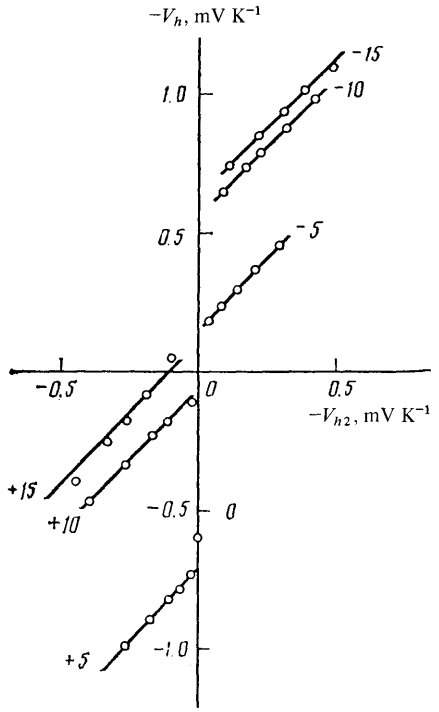


Figure 2. Dependence of V_h on $(\delta\Phi_2/\delta T)_q$ for different electrode charges (indicated in the figure in μC cm^{-2}); the continuous lines correspond to Eqns.(25) and (26).[25]

The kinetics of the LTJ signal in dilute solutions have been investigated in a study[6] where it has been shown that a slow increase in $V_h(t)$ takes place in the vicinity of the ZCP and that the characteristic time of the increase rises in inverse proportion to the electrolyte concentration. The theoretical description of the relaxation of the diffuse part of the EDL, based on the simultaneous solution of the continuity equations for the currents due to ions of both signs and the Poisson equation, shows that the spatial-time variation of the charge density is described by the same equation as the relaxation of the Debye atmosphere.[26] For a low initial change in the potential, its decrease takes place with a characteristic time given by

$$\tau_d = \varkappa^2 D, \quad \varkappa^2 = \frac{8\pi e^2 a}{\varepsilon kT} , \qquad (28)$$

where $\varkappa^{-1}$ is the Debye length and D the coefficient of the dipolar diffusion of ions. The characteristic EDL relaxation times in the vicinity of the ZCP, measured by Benderskii et al.,[6] increase from 10 to 50 ns if the electrolyte concentration is reduced from 0.01 to 0.002 M, i.e. the $\tau_d(a)$ relation agrees with Eqn.(28).

As stated above, in the classical EDL theory it is assumed that the properties of its dense part in the absence of specific adsorption are independent of the electrolyte concentration. To test this principal hypothesis of the theory, measurements have been made[27] by

the LTJ method of the $V_h(E)$ relation in KF solutions at concentrations ranging from 1 to 12 M. A characteristic feature of this electrolyte[28] is the independence of the ZCP of the salt concentration and the insignificant increase in the differential capacitance for high negative charges ($q < -15$ μC cm^{-2}). Its more appreciable increase at $q \geqslant 0$ is attributed to the partial dehydration of the fluoride ions in such concentrated solutions, which dimishes the effective thickness of the EDL. According to Benderskii et al.,[27] the $V_h(E)$ and $S^\sigma(q)$ relations are also relatively insensitive to the KF concentration. Furthermore, the relaxation characteristics of the EDL hardly change, which means that the aqueous layer in the inner part of the EDL remains unaltered even at such high concentrations of the specifically non-adsorbable ions where the number of molecules in the bulk of the solution is no longer sufficient for the formation of the hydration shells, which are produced in dilute solutions.

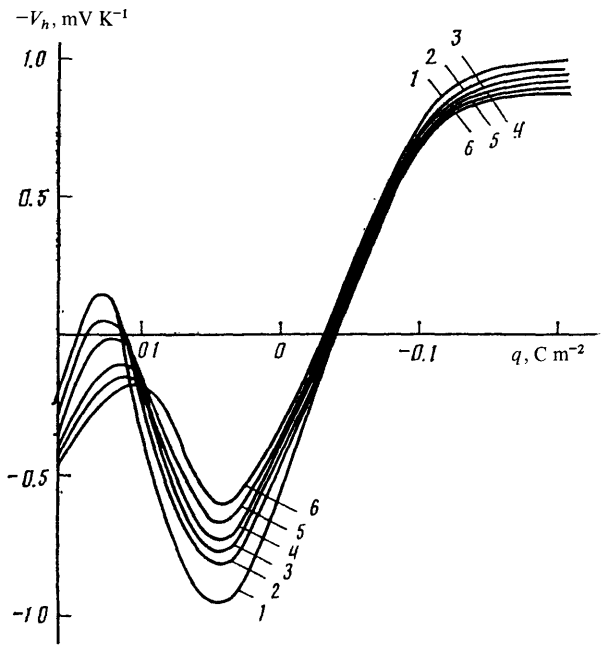


Figure 3. The $V_q(q)$ relations at different temperatures (°C): 1) 10; 2) 20; 3) 30; 4) 40; 5) 50; 6) 60; mercury electrode in aqueous 0.9 M NaF solution.[9]

At first sight, the agreement with experiment of the simple EDL theory over such a wide range of electrolyte concentrations is surprising bearing in mind that concentrated solutions are not described by the Debye–Hückel theory, which constitutes the basis of the simple EDL theory. The main reason for the observed agreement is apparently the independence of the structure of the dense part of the EDL of the electrolyte concentrations, by virtue of which a sharp dependence of the dielectric characteristics on the concentration and size of the ions, predicted by modern electrolyte models (see Carnic and Torrie's review[29]), is not manifested in the observed integral characteristics of the EDL.

VI. THE EXCESS ENTROPY AND HEAT CAPACITY OF THE DENSE PART OF THE ELECTRICAL DOUBLE LAYER

As can be seen from Figs.3 and 4, in the absence of specific adsorption, the $V_h^{M-2}(E)$ curves for the mercury electrode have three ZRP, implying that the dependence of the excess entropy of formation of the dense part of the EDL on the electrode charge is characterised by a minimum and two maxima in the vicinity of which there is a sharp increase in the relaxation time. With increase in temperature, the $S^\sigma(q)$ curves becomes gradually symmetrical relative to the $q = 0$ axis: the maximum and minimum in S^σ in the vicinity of $q > 0$ disappear above 40 °C, while the maximum at $q < 0$ shifts from -4.2 to -3.6 μC cm^{-2} in the range 0–65 °C.[8,9]

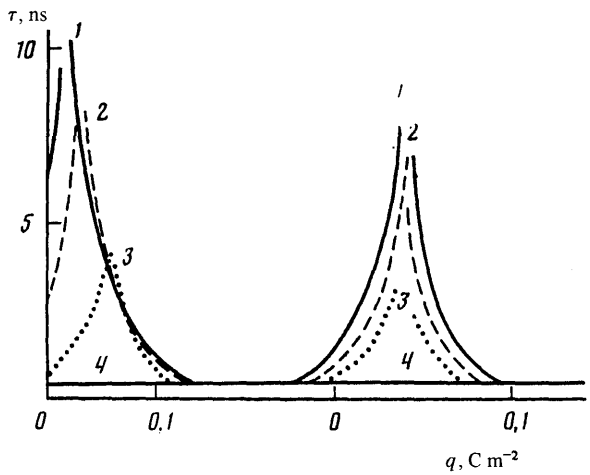


Figure 4. $\tau(q)$ relations at different temperatures °C: 1) 10; 2) 20; 3) 40; 4) 60; mercury electrode in aqueous 0.96 M NaF solution; accuracy of the measurement of τ to within 2 ns.[9]

The excess heat capacity of formation of the dense part of the EDL, given by

$$c^\sigma = T\left(\frac{\partial S^\sigma}{\partial T}\right)_{q,a} . \qquad (29)$$

has been found[9] from the temperature variation of $S^\sigma(q)$. The $S^\sigma(q)$ and $c^\sigma(q)$ relations at different temperatures are presented in Fig.5.

The properties of the dense part of the EDL are determined by the monolayer of the dipolar solvent molecules adsorbed on the metal.[1] By virtue of the interaction of the dipoles with the EDL field and with one another and also by virtue of specific adsorption forces, this two-dimensional layer undergoes orientational ordering. The orientation of the dipole depends on the field strength in the inner part of the EDL, i.e. on the charge of the electrode, which leads to a non-linear $q(E)$ relation. The decrease in the potential within the dense part of the EDL can be represented in the form

$$\varphi = \frac{\delta}{\varepsilon} q + \frac{Np}{\varepsilon} f(q) , \qquad (30)$$

where δ is the effective thickness of the dense part of the EDL, ε is its dielectric constant in the absence of orientational polarisation, determined by the molecular polarisability of the solvent molecules, and N and p are the surface density and the dipole moment of the

solvent molecules. The function $f(q)$ characterises the degree of orientation of the dipoles. In strong electric fields (for $q \to \pm\infty$), the dipoles are fully oriented and $f = \pm 1$, so that, for constant δ/ε and Np/ε, f becomes a linear function of q. According to Trasatti,[30,31] the $\varphi(q)$ curves for aqueous electrolyte solutions are not only linear but also have the same slope for different *sp* metals in the region of high negative potential ($q \leqslant -10$ μC cm^{-2}), which indicates the universality of Eqn.(30).

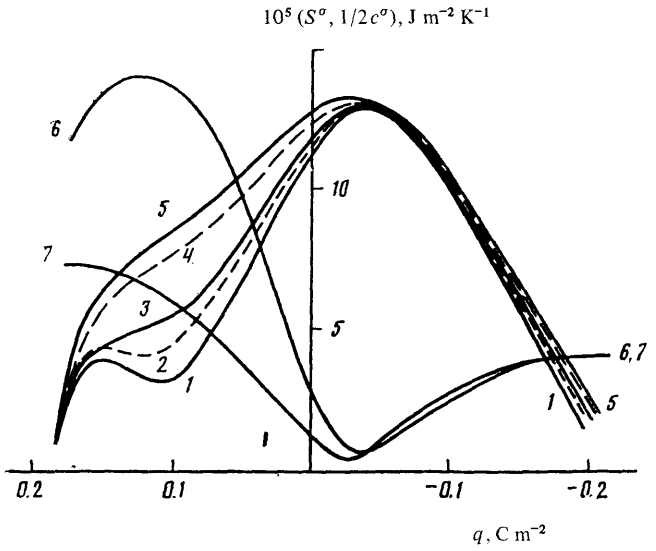


Figure 5. $S^\sigma(q)$ (curves *1*–*5*) and $c^\sigma(q)$ (curves *6* and *7*) relations at different temperatures (°C): 1) 10; 2) 20; 3) 40; 4) 60; 5) 70; 6) 15; 7) 65; mercury electrode in aqueous 0.96 M NaF solution.[8]

In the initial model of the two-dimensional,[32] two possible dipole orientations were considered. In this case f is determined by the numbers of dipoles oriented along the electric field and in opposition to it and in the case of isolated dipoles is described by the relation

$$f = \frac{N_+ - N_-}{N} = \tanh u, \; u = \frac{p}{\varepsilon kT}(q - q^*) \; . \qquad (31)$$

For $q = q^*$, both orientations are equally probable and $f = 0$. The characteristic charge q^* is non-zero as a consequence of the difference between the free energies of adsorption for the two orientations. The potential at which $q = q^*$ is identical with the ZRP, because the orientational entropy is a maximum for $N_+ = N_-$. The $\tau(q)$ relation is described by the expression

$$\tau = \frac{\tau_0}{\cosh u} \qquad (32)$$

and also has a maximum equal to τ_0 at $q = q^*$. Thus in the two states model the ZRP is universal for all metals for which Eqn.(30) holds and corresponds to the absence of a dipole potential jump, i.e. to $f = 0$.

Since the two states model does not lead to a quantitative description of the differential capacitance curve (*CE* curves) at different temperatures, models have been developed with a larger number of states (see, for example, Refs.33–38) taking into account the possibility of the formation of dipolar associated species in the two-dimensional layer.‡ In the presence of n states of the $2d$ layer, the number of ZRP is at least $n - 1$ regardless of the characteristics of these states.[39] Each of them corresponds to a local entropy maximum determined by the equality of the probabilities of two definite states. For example, in the three states model[37] (two opposite orientations of the dipoles and their aggregates which have no moment), the $S^\sigma(q)$ relation should have two maxima corresponding to the conversion of the dipoles into aggregates. Curves *1* and *2* shown in Fig.5 can be regarded as experimental proof of the existence of at least three states of the water dipoles in the two-dimensional layer. However, the $\tau(q)$ relations do not agree with the hypothesis of the existence in the two-dimensional layer of isolated water molecules and their low-molecular-weight associated species, because in this case, as in the two level model, the decrease in $\tau(q)$, like that in $S^\sigma(q)$, is determined by u and may occur over a wide range of q values. The pronounced $\tau(q)$ relation is clearly not described by Eqn.(32) and indicates a cooperative character of the rearrangement of the $2d$ layer at the ZRP, which is not described by the models put forward in the literature.[32–39] It has been suggested[8,9] that, in the region located between the ZRP ($q_1 < q < q_2$, q_1 and q_2 correspond to the ZRP), there exists below 40 °C an ordered state of the water molecules of the type of two-dimensional ice, which is decomposed by the electric field at the ZRP as a result of the reorientation of the dipoles. The disruption of the antiferromagnetic ordering in strong magnetic fields is an analogue of this process.[40] The free energy of an ordered state of the antiferroelectric type increases with increase in $|q - q_0|$ (q_0 corresponds to the minimum in S^σ) and a structural phase transition to a paraelectric state, whose energy diminishes with increase in $|q - q_{1,2}|$, occurs at the points q_1 and q_2. Above 60 °C, the paraelectric state exists at all values of q, which is indicated by the disappearance of the ZRP, corresponding to q_1 and q_0, and of the $\tau(q)$ peaks. The $S^\sigma(q)$ and $c^\sigma(q)$ relations in this state agree with relations calculated in terms of the molecular field approximation[41] for reasonable values of the parameters: $p = 1.3$ D and $N = 2 \times 10^{15}$ cm^{-2}.[9] The fluctuation theory of phase transitions has been used for the description of the $2d$ layer at lower temperatures.[8,9] The singular part of the free energy in the critical region Φ_S is a function of the parameter $A(T - T_c)$,[43] in which A and the critical temperature T_c depend on $(q - q_0)^2$, provided that the order parameter $l \propto (q - q_0)^2$. The equation for the critical values, $A(T - T_c) = 0$, has two roots:

$$q_{1,2} = q_0 \pm \Delta(T) \; . \qquad (33)$$

The $\Phi_S(q)$, $l(q)$, and $\tau(q)$ relations are determined by the values of the universal critical indices:

$$\Phi_S \propto U^{2-\alpha}, \; l \propto U^{\beta}, \; \tau^{-1} \propto \frac{\partial^2 \Phi_S}{\partial l^2} \propto U^{2-\alpha-2\beta},$$
$$U = B(T)\,|\,(q - q_0)^2 - \Delta^2(T)\,| \; , \qquad (34)$$

where $B(T)$ is a non-singular function of temperature. It follows from Eqn.(34) that the increase in the relaxation time should occur at the points q_1 and q_2, where the order parameter l becomes zero,

‡ Despite the difference between the numbers of states and the values of the parameters (the adsorption energies, the dipole moments, N and ε), all these models make it possible to describe satisfactorily the *CE* curve at different temperatures, which, rather than indicating the reliability of these models, is more likely to be evidence for the insensitivity of the experimental data to their choice, associated with the large number (5–7) of parameters, which are in essence adjustable.

and $S^{\sigma}(q)$ is a maximum. In agreement with the hypothesis of the universality of the critical indices, the values of $\gamma = 2 - \alpha - \beta$ are identical at the points q_1 and q_2 and amount to approximately 0.7.

It is noteworthy that at the critical points the maxima in the second derivatives of Φ_S with respect to q and T (the differential capacitance, V_h, and c^{σ}), which are the usual signs of second-order phase transitions, are not observed. The absence of singularities on the curves indicated can apparently be accounted for by the fact that they are determined by the low critical index α, which may be close to zero for two-dimensional systems.[42] On the other hand, the $\tau(q)$ singularities are determined by the larger critical index γ and for this reason are easier to observe experimentally. Furthermore, the ordered state of the non-commensurate lattice on the surface of the liquid metal is most likely to be appreciably converted into an amorphous form, which widens the region of the transition. This is indicated, in particular, by the higher heat capacity of the antiferroelectric state compared with the paraelectric state (Fig.5).

The phase transitions in the two-dimensional layers have been the subject of vigorous research (see Vilches' review[44]) and in this connection one may point to a series of systems whose behaviour is close to that of the new EDL model proposed by Benderskii and co-workers.[8,9] For example, the transition from the planar to the perpendicular oreintation of nitrogen[45] and ethane[46] molecules as well as the dimerisation of nitric oxide[47] have the character of phase transitions. In most cases the lattice parameteers of two-dimensional crystals close to the three-dimensional parameters are incommensurate with the lattice of the support. On the basis of these data, one can hardly be surprised that water molecules on the surface of metals are capable of forming an ordered structure.

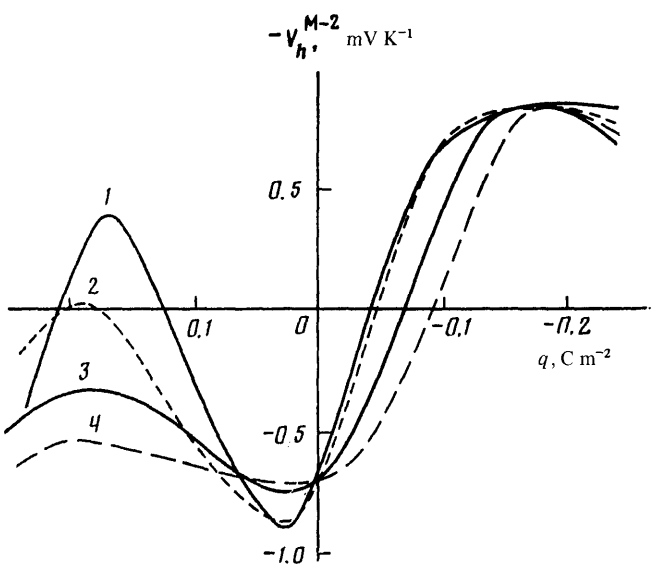


Figure 6. $V_h^{M-2}(q)$ relations at the interface between the mercury electrode and 1 M aqueous solutions of different salts: 1) KF; 2) KCl; 3) KBr; 4) KI.[50]

The values of τ in the vicinity of the ZRP, measured[7] for different *sp* metals, amount to $10^{-7}-10^{-8}$ s, while in the ordering region they do not exceed 3×10^{-8} s. Comparison of these values with the dipolar relaxation times in liquid water ($\sim 10^{-11}$ s) and in ice crystals ($\sim 10^{-5}$ s at 0 °C) makes it possible to infer the mobility of water molecules at the interface. The rotation of dipoles in ice crystals is due to the translational movement of Bjeruum defects.[48] In the cavities within vitreous ice, the rotational relaxation time at -10 °C is approximately 10^{-10} s.[49] Presumably at $q \leqslant 0$, where water molecules form M–O bonds with the surface, the rotation of the dipoles does not entail the rupture of these bonds and takes place similarly to relaxation in liquid water and not in the crystal.

In conclusion of this Section, we shall deal with the question of the correspondence of the ZRP and the potential at which there is no dipole jump. As stated above, these potentials agree only in the two state model. For $n > 2$, in the general case none of the ZRP correspond to $f = 0$ and the identification of the ZRP for $q < 0$ with the potential at which $f = 0$, postulated in a number of investigations,[22,30,31,35] requires a more careful study, like the determination of the dipole jumps at the ZCP based on it. The latter jumps are regarded as a measure of the hydrophilicity of metals.[1,30] The difference between ZCP and ZRP (for $q < 0$) diminishes with increase in hydrophilicity in the sequence Hg, Pb, Bi, Cd, Ga. The values of $-q_2$, corresponding to the ZRP, decrease in the same sequence as a result of the increase in the slope of the qE curves in the region of low values of q.[7]

VII. ADSORPTION OF ANIONS

The $V_h(E)$ curves for aqueous KCl, KBr, and KI solutions (Fig.6) differ in the region of the adsorption of halide ions.[50] In analysing these curves, it is necessary to take into account the contribution to $(\partial\varphi_2/\partial T)$ by the temperature coefficients of the excess adsorbed surface anions:

$$\left(\frac{\partial q_1}{\partial T}\right)_q = q_1 \frac{\Delta G_a}{RT}(1 + B_2\Gamma_i)^{-1}, \qquad (35)$$

where $q_1 = F\Gamma_i$, Γ_i is the surface excess, ΔG_a the free energy of adsorption, and B_2 the second virial coefficient, which is known from electrochemical data.[51]

The $S^{\sigma}(q)$ relations, found taking into account the correction defined by Eqn.(35), are illustrated in Fig.7. The adsorption of anions leads not only to a decrease in S^{σ} but also to the disappearance of the ZRP in the region $q > 0$, which is accompanied by the simultaneous disappearance of the relaxation time peak. The $\tau(q)$ peak is retained in 1 M KCl solution at $q < 0$ but its width becomes smaller than in the fluoride solution. In the region of the adsorption of BR^- and I^-, an increase in τ to 5–6 and 8–10 ns respectively is observed. The disappearance of the $S^{\sigma}(q)$ minimum shows that the specific adsorption of ions disrupts the ordered state of the two-dimensional layer, in particular as a consequence of the change in the orientation of the dipoles participating in the formation of the hydration shells of the adsorbed ions.§ Within the framework of the theory,[42] the introduction of impurities into the 2*d* layer decreases the critical transition temperature, which is taken into account in Eqn.(33) by the function ΔT, which depends on the degree of coverage θ:[54]

$$\frac{\Delta(T, \theta)}{\Delta(T, 0)} = \begin{cases} 1 - \theta, & \theta \ll \theta_c, \\ |\theta - \theta_c|^{t_c}, & \theta \propto \theta_c, \end{cases} \qquad (36)$$

§ It has been suggested[52,53] that the hydration shells of ions do not undergo major distortion on adsorption. Quantum-chemical calculation[53] has shown that the disposition of the ion and free water molecules in a single plane corresponds to the minimum energy of the hydrated Cl^- anion.

where θ_c is the permeation threshold at which the transition disappears and t_c is the critical index of the breakdown of the transition. In this model the disordering of the two-dimensional layer takes place, judging from the disappearance of its cooperative rearrangement at the ZRP already at comparatively low degrees of coverage ($-q_1 = 3-5$ μC cm^{-2}) corresponding to average distances of 2–3 nm between the adsorbed ions. The EDL relaxation time in the adsorption region is apparently determined by the movement of the adsorbed ion and its higher value compared with the Debye relaxation time characterising the relaxation of ions in the diffuse part of the EDL (see above) reflects the decrease in the mobility of ions and their hydration shells on adsorption.

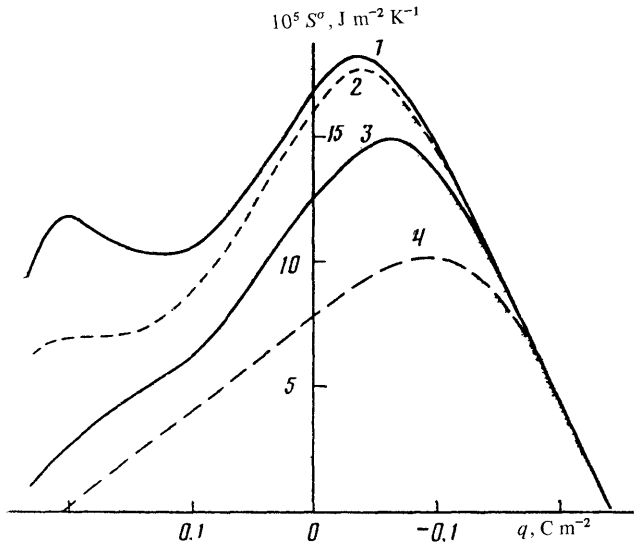


Figure 7. $S^\sigma(q)$ relations at the interface between the mercury electrode and 1 M aqueous solutions of different salts: 1) KF; 2) KCl; 3) KBr; 4) KI.[50]

The values of B_2 can be found by comparing the $S^\sigma(q)$ curves in solutions of specific adsorbable ions and in the solution where there is no adsorption. The values of B_2 have been obtained[50] for Br^- and I^- (2.2×10^{-14} and 3.3×10^{-14} cm^2 respectively), which agree with other data,[20,55] and the relation between B_2 and q for Cl^-, noted by Charles et al.,[20] has been confirmed. Because of the repulsion of the adsorbed ions, their distribution on the surface with increasing Γ_i ceases to be random, which entails a decrease in S^σ. The increase in the electric field strength of the EDL, i.e. in q, causes disordering in the distribution of the adsorbed ions in the two-dimensional layer, i.e. a decrease in B_2.

The negative Gibbs adsorption of chloride ions at the interface between the mercury electrode and concentrated LiCl solutions, in which the activity of the salt changes almost by three orders of magnitude when its concentration c_S is raised from 1 to 12 M, ensuring a broad region in which the thermodynamic relations (19) and (21) can be tested, has been investigated[56] by the LTJ method. With increasing c_S, the $V_h(E)$ curves shift to the region of more negative potentials (Fig.8), the ZRP being located in the region more negative by 0.15–0.30 B than the ZCP, the difference between these potentials increasing, i.e. the maximum entropy occurs for more negative charges.

The shift of the ZRP is accompanied by a shift of the EDL relaxation region, the width of the $\tau(E)$ peak decreasing and the values of τ increasing. The $(\partial S^\sigma/\partial \ln c)_{q,T}$ for a concentrated LiCl solution do not agree with Grahame's theory not only in magnitude but also in sign. The temperature coefficients of the surface excess amounts found from Eqn.(19) for $q < -5$ μC cm^{-2} are $(\partial\Gamma_\pm/\partial T)_q > 0$ [according to Grahame's theory $(\partial\Gamma_\pm/\partial T)_q < 0$] and their absolute values are more than an order of magnitude greater than expected. Negative values of the theoretical coefficients are associated with the fact that an increase in temperature tends to equalise the ion concentrations in the solution and in the double layer. The observed positive values of $(\partial\Gamma_\pm/\partial T)_q$ imply that the excess surface amounts of ions of both signs are negative. Thus the sign of $(\partial\Gamma_\pm/\partial T)_q$ is a direct consequence of the negative adsorption of the salt for $q < 0$ noted in the literature.[28,57] In Grahame's theory the presence of non-adsorbable ions at the interface and in the bulk of the solution for $q = 0$ is assumed to be equally probable. Evidently this approximation breaks down if the hydration conditions in the bulk phase and at the interface are different. Such difference arises in concentrated electrolyte solutions where the number of water molecules is insufficient for the construction of the hydration shells of the ions.

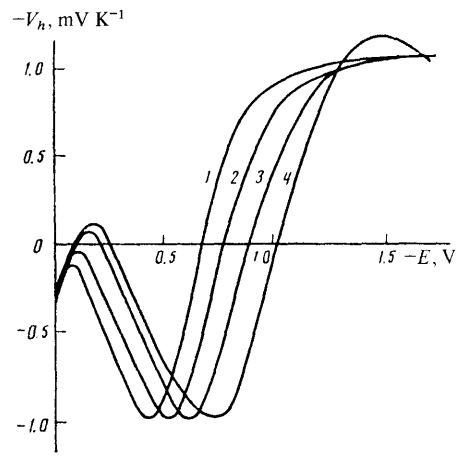


Figure 8. $V_h(E)$ relations at the mercury–concentrated aqueous LiCl solutions interface; LiCl concentration (M): 1) 1; 2) 4; 3) 8; 4) 13.7.[56]

In contrast to Grahame's theory, there is a broad range of values of q where the increase in c_S diminishes S^σ as a consequence of the ordering of the ionic component [of the EDL?], possibly on formation of a layered structure.[58] The retention of the form of the $V_h(q)$ curves and the EDL relaxation in the region of the ZRP for high values of c_S implies that water molecules remain in the inner part of the EDL even in very concentrated solutions which is also due to the negative adsorption of the salt.

If the water layer were located between the outer and inner Helmholtz planes, the shift of the ZRP should have corresponded to the constancy of $q + q_1$ and the charge at the ZRP should have increased with increase in $-q_1$, whereas in fact q diminishes. This means that the layer of water molecules is located between the metal and the inner Helmholtz plane (the plane corresponding to the maximum approach by the adsorbed ions). This hypothesis agrees with the data indicated above demonstrating a comparatively small deformation of the hydration shells of ions on adsorption.

VIII. ADSORPTION OF ORGANIC SUBSTANCES

The principal difference in the LTJ in the case of the adsorption of organic surfactants (OS) consists in the constancy of their surface excess Γ under the conditions of the pulse heating of the electrode, which is responsible for the short duration of the heat pulse compared with the time of attainment of the adsorption-desorption equilibrium and follows directly from the frequency dependence of the initial capacitance $C_1 = (\partial\Gamma/\partial E)(\partial\Gamma/\partial q)^{-1}_{T,c}$. This capacitance is observed at frequencies below 10^4 Hz,[59] while the times of the LTJ measurements do not exceed 10^{-6} s. For this reason, LTJ refers to non-equilibrium conditions relative to the bulk of the solution. On the other hand, in the heated layer near the electrode, there is sufficient time for diffusion to establish equilibrium between the surface excess and the OS concentration, i.e. the LTJ is measured under conditions described by the thermodynamic potential corresponding to the q, T, and Γ variables. For this potential, we have

$$V_h = \left(\frac{\partial\varphi}{\partial T}\right)_{q,\Gamma} = -\left(\frac{\partial S^\sigma}{\partial q}\right)_{T,\Gamma} . \tag{37}$$

In Eqn.(7), the component of V_h due to the thermal diffusion of the OS is neglected. In order to determine S^σ, it is necessary to convert the values of V_h into the derivative $(\partial S^\sigma/\partial q)_{T,c}$ measured at a constant OS volume concentration and not at a constant Γ. This change in the variables q, T, and μ leads to the relation

$$\left(\frac{\partial\varphi}{\partial T}\right)_{q,\Gamma} = \left(\frac{\partial\varphi}{\partial T}\right)_{q,c} + \left(\frac{\partial\varphi}{\partial \ln c}\right)_{q,T}\left(\frac{\partial \ln c}{\partial T}\right)_{q,\Gamma} , \tag{38}$$

which has been obtained[60] by the standard method involving the transformation of the variables of the thermodynamic functions[43] (p.83). On the assumption that the adsorption isotherm is congruent relative to the electric variable,[59] it can be expressed in the form

$$c\cdot\exp(-G_a/RT) = f(\Gamma) , \tag{39}$$

where ΔG_a is the free energy of adsorption, which depends on q but is independent of Γ. It follows from Eqns.(38) and (39) that

$$\left(\frac{\partial S^\sigma}{\partial q}\right)_{T,c} = -V_h + \frac{\Delta G_a}{T}\left(\frac{\partial\Gamma}{\partial q}\right)_{T,c} . \tag{40}$$

The surface pressure[2]

$$\Pi = RT\Gamma_m f(\Gamma) , \tag{41}$$

where Γ_m is the maximum coverage, corresponds to the isotherm (39). According to Everett,[61] we have

$$\left(\frac{\partial\Pi}{\partial T}\right)_\Gamma = -\Gamma_m\theta^2\left(\frac{\partial S^\sigma}{\partial\theta}\right)_{T,c} , \tag{42}$$

where $\theta = \Gamma/\Gamma_m$ is the degree of coverage. A relation between ΔG_a and the molar entropy of adsorption S_a follows from Eqns.(39) and (42):

$$S_a = \left(\frac{\partial S^\sigma}{\partial\Gamma}\right)_{T,c} = S_a^0 + \frac{\Delta G_a}{T} - R\ln c , \tag{43}$$

where S_a^0 is the part of the molar entropy of adsorption determined by the change in the internal degrees of freedom of the adsorbate. If structural changes in the adsorbate molecules, caused by their interaction, take place in the course of surface coverage, S_a^0 is a function of Γ. On substituting Eqn.(43) in Eqn.(40) and integrating with respect to q taking into account the fact that desorption takes place at high negative electrode potentials ($\Gamma = 0$ at $q \to -\infty$), we find

$$S^\sigma = S_1^\sigma + \Delta + S_\infty - R\Gamma\ln c , \tag{44}$$

where

$$S_1^\sigma = \int_0^\Gamma S_a^0\,d\Gamma, \quad \Delta = \int_{-\infty}^{q}\frac{\Delta G_a}{T}\left(\frac{\partial\Gamma}{\partial q}\right)_{T,c} dq . \tag{45}$$

S_∞ is the integration constant. Integration of Eqn.(40) under the same conditions yields

$$S^\sigma = S_h + \Delta + S_\infty , \tag{46}$$

where

$$S_h = -\int_{-\infty}^{q} V_h(q)\,dq . \tag{47}$$

Eqns.(44) and (46) establish a relation between S_h (the integral of V_h) and S^σ and its structural components S_1^σ:

$$S_h = S_1^\sigma - R\Gamma\ln c . \tag{48}$$

It follows from Eqn.(48) that the $S_h(q)$ relation describes the change in the EDL structure and is independent of the configurational component S^σ, which is given by $S_2^\sigma = \Delta - R\Gamma\ln c$. Since S_2^σ usually exceeds S_1^σ severalfold,[60] the $S_h(q)$ curves, i.e. the LTJ data, contain more information permitting the discovery of the structural changes in the EDL than the $S^\sigma(q)$ curves. The logarithmic dependence of S_h on the OS concentration is due to the definition of S^σ as the difference between the entropies of the components on the surface and in the bulk phases in the standard state, the transition to which corresponds to a change in $S = S^0 - R\ln c$. The above thermodynamic analysis is valid when the function $S^0(q)$ is continuous, which can be tested experimentally. If there are no jumps in S^σ in the region of adsorbability, the relation

$$\int_{-\infty}^{+\infty}[V_h(q, 0) - V_h(q, \Gamma)]\,dq = 0, \tag{49}$$

which follows from the condition that the values of S^σ are identical regardless of adsorbability of all OS concentrations, is valid.

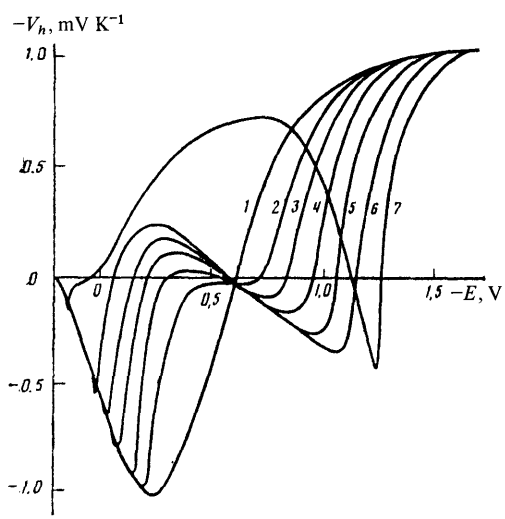


Figure 9. $V_h(E)$ relations at the interface between the mercury electrode and 1 N aqueous Na_2SO_4 solution with added n-pentyl alcohol at concentrations of 0, 5×10^{-3}, 1×10^{-2}, 1.5×10^{-2}, 3×10^{-2}, 5×10^{-2}, and 0.15 M (curves *1*–*7* respectively).[62]

The adsorption of aliphatic n-alcohols ranging from C_3 to C_6 on the mercury electrode has been investigated by the LTJ method.[60,62] Typical $V_h(E)$ relations are presented in Fig.9. With increase in the OS concentration, the deviations from the background V_h^0 curve

increase. For $\Gamma \cong \Gamma_m$, a second $V_h(E)$ section, with a constant positive slope corresponding to a quadratic $\Delta G_a(q)$ relation, appears. In the region of adsorbability, there are three ZRP.

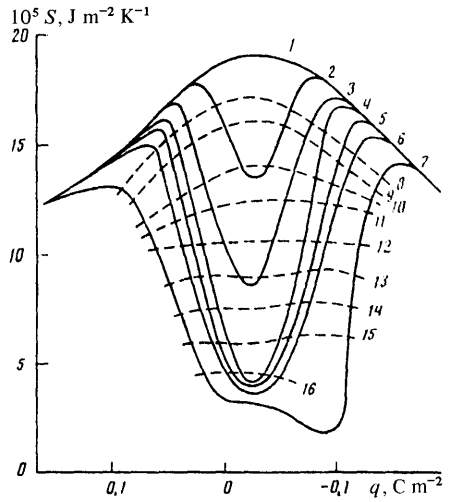


Figure 10. $S_h(q)$ relations in the adsorption of n-pentyl alcohol on the mercury electrode from aqueous 1 N Na_2SO_4 solution with the same OS concentrations as in Fig.9; the dashed curves *8—16* represent the $S^{\sigma}_{\Gamma}(q)$ relations for constant degrees of coverage ranging from 0.1 to 0.9 in 0.1 steps respectively.[60]

The extreme two of these potentials coincide with the potentials of the maxima on the $C(E)$ differential capacitance curves and correspond to degrees of coverage $\theta_c \cong 0.5$. The $V_h(E)$ curves for different c intersect at approximately one point corresponding to the maximum adsorption potential. A typical $S_h(q)$ relation is illustrated in Fig.10 and demonstratres the presence of two maxima and a minimum in the structural entropy of the EDL. The validity of Eqn.(48) has been verified.[60] The values of Γ_m found from the linear sections of the $S_h(\ln c)$ curves agree with the results of electrochemical measurements.[59] Fig.10 also presents the $S^{\sigma}_h(q)$ relations for constant Γ, calculated from the $S_h(q, c)$ curves by Eqns.(45) and (46) using the parameters of the adsorption isotherms taken from Damaskin et al.[59] The change in the form of the curves with increasing Γ shows that, for $\theta \gtrsim 0.4$, the adsorption of aliphatic alcohols cannot be regarded as the substitution of isolated water molecules by isolated OS molecules. The cooperative character of the rearrangement of the EDL is manifested by the sharp increase in relaxation time near the ZRP corresponding to the S_h maxima.¶ Theoretical analysis of the $V_h(E)$, $C(E)$, and $\tau(E)$ relations for the adsorption of OS has been carried out[63] on the basis of the ideas concerning the two-dimensional second-order phase transitions examined in Section V of this review. According to the present authors,[60,62] Eqn.(49) holds only at low concentrations of n-pentyl ($< 5 \times 10^{-2}$ M) and n-hexyl ($< 3 \times 10^{-2}$ M) alcohols. For higher values of c, a sharp decrease in V_h (down to $V_h < 0$) is observed and, after the break at the minimum, there is just as sharp an increase (to $V_h > 0$). The appearance of V_h peaks (Fig.9), corresponding to jumps in S_h (Fig.10), indicates the occurrence of first-order phase transitions.

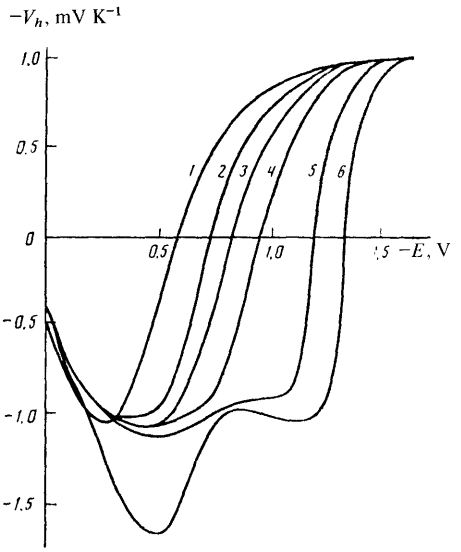


Figure 11. $V_h(E)$ relations for the adsorption of phenol on the mercury electrode from aqueous 0.5 M Na_2SO_4 solution; the phenol concentrations are 0, 4×10^{-3}, 2×10^{-2}, 4×10^{-2}, 0.1 and 0.4 M for curves *1—6* respectively.[64]

The LTJ method has been used[64] to investigate the adsorption of phenol and 1,3,5-trihydroxybenzene (THB). The choice of phenol was dictated by the fact that, according to Damaskin et al.[65] and Sarangapani and Venkatesan,[66] its adsorption, like that of the majority of aromatic OS, is possible in two orientations—planar and perpendicular, the second of which occurs at fairly high concentrations ($> 4 \times 10^{-5}$ M) in the vicinity of the ZCP, while the first obtains at high positive potentials.[67] Apart from the adsorption-desorption maxima, jumps in differential capacitance have been observed[66,68] in the adsorption of THB on mercury and were attributed to the formation of two-dimensional crystals of the THB dihydrate. The $V_h(E)$ curves for the above compounds are presented in Figs.11 and 12. The potentials for the $C(E)$ maxima coincide with the ZRP at different OS concentrations and are also characterised by EDL relaxation time peaks (Fig.13). In contrast to the systems examined previously (Fig.4), the $\tau(E)$ peaks are highly asymmetric. In the region of abrupt changes in capacitance in the course of the adsorption of THB, V_h peaks arise. The values of τ in the range of E between the ZRP and the V_h peak is much greater than in the supporting electrolyte and amounts to approximately 30 ns. In the vicinity of the V_h peak, i.e. in a first-order phase transition, there is

¶ The S^{σ}_{Γ} relations were known previously only for low degrees of coverage ($\theta < 0.4$) of the mercury electrode by thiourea.[23] It has been concluded[23] that S^{σ}_{Γ} is an additive function of the degree of coverage, consisting of two contributions, associated with the adsorbed water and OS molecules. LTJ data have shown that this conclusion cannot be extended to the range of higher coverages.

a sharp decrease in τ down to values less than 10 ns. It has been suggested[64] that the order of the phase transitions in the EDL can be determined from the following features of the $C(E)$, $V_h(E)$, and $\tau(E)$ curves (see Table). The simultaneous appearance of $C(E)$ peaks and $V_h(E)$ zero values at the second-order phase transition points follows directly from the form of the singular component of the thermodynamic potential (34) when Δ is independent of T. The constancy of the degree of coverage at which the transition takes place ($\theta_c \cong 0.5$) indicates its similarity to transitions of the order–disorder type; when $\theta < \theta_c$, random coverage of the nodes (adsorption sites) takes place and, when $\theta \cong \theta_c$, a state with a short-range order in their distribution arises. Such transitions in planar lattices have been investigated in fair detail.[44–47,69,70] The critical values of θ_c, corresponding to the formation of "an infinite cluster" of occupied nodes (the permeation threshold), depends on the lattice geometry, the configuration of the molecules, and their orientation in adsorption.[71,72]

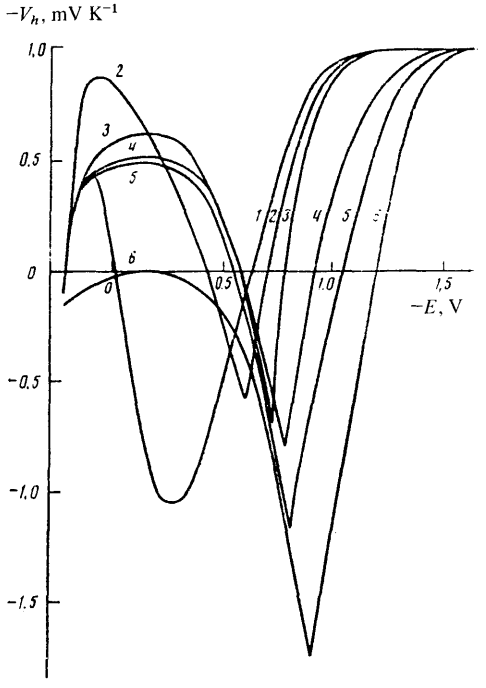


Figure 12. $V_h(E)$ relations for the adsorption of 1,3,5-trihydroxybenzene on the mercury electrode from aqueous 0.5 M $LiClO_4$ solution with OS concentrations of 0, 4×10^{-5}, 10^{-3}, 5×10^{-3}, 2×10^{-2}, and 0.1 M for curves *1*–*6* respectively.[64]

Although some of the features enumerated in the Table can be poorly expressed (for example, in the adsorption of aliphatic alcohols jumps in τ are not observed in first-order transitions, while in the adsorption of phenol one observes minima at low values of c instead of negative v_h peaks), nevertheless the combination of LTJ data and electrochemical measurements makes it possible to establish the occurrence and order of the phase transitions in the EDL when the potential is varied.

A characteristic feature of mixtures of water and aliphatic compounds with a terminal polar group (amphiphiles) is the formation of liquid crystal phases due to the fact that the equilibrium packing of the amphiphile molecules should ensure the shielding of the hydrophobic hydrocarbon chain from water. According to the cT diagram for amphiphile–water mixtures,[70] an increase in the amphiphile concentration entails a transition from a solution of isolated molecules to a micellar phase. On further increase in c, the micellar phase is converted into liquid crystal mesophases—hexagonal and lamellar, which are then converted into an amphiphile crystal. The micellar phase–mesophase transitions and the transitions between the mesophases can be both of the first and second order, while the mesophase–crystal transition is usually a first order transition of the type of fusion. Presumably structures with different disposition of the adsorption sites and different packing of the hydrocarbon chains are formed at the interface between the metal and the aqueous solution of amphiphiles. Second-order phase transitions are apparently associated with the formation of two-dimensional mesophases containing the oriented OS and water molecules. The first-order phase transition can be attributed to the formation of OS crystals or mixed OS–water crystals at the interface. In the adsorption of aromatic alcohols, a mesophase is formed in second-order phase transitions, is less ordered (has a higher entropy) for a higher density of the OS, and, judging from the relaxation times of approximately 10^{-8} s, contains water molecules capable of changing their orientation as the temperature is varied. In the first-order phase transition, this mesophase is converted into two-dimensional crystals in which the OS and water molecules are linked by hydrogen bonds. According to X-ray diffraction data,[73] similar planar packing is characteristic of phenol and THB hydrates.

Manifestation of phase transitions in different relations.

Relation	Order of phase transition	
$C(E)$	jump	maximum*
$V_h(E)$	peak	zero
$\tau(E)$	jump	peak

*It may be that the finite $C(E)$ values at the maxima on the CE curve are due to the fairly large amplitudes and high modulation frequencies of the electrode potential in the measurements, while the values corresponding to thermodynamic equlibrium are singular at the transition points.

The determination by the LTJ method of the transition potentials in solutions with different OS concentrations leads to the possibility of constructing cE phase diagrams for the adsorption layers. Fig.14 presents as examples diagrams of this kind for solutions of n-pentyl alcohol and THB. For low values of c, a second-order transition from a two-dimensional solution to a water crystal (line II) occurs in the region of adsorbability. With increase in c, two second-order transitions occur in the first case, bounding the region of existence of the mesophase ($\theta \geqslant \theta_c$). On further increase in the OS concentration, first-order transitions (line I) from the mesophase to the crystal are observed. In the case of THB, the latter exists up to the maximum attainable values of c.

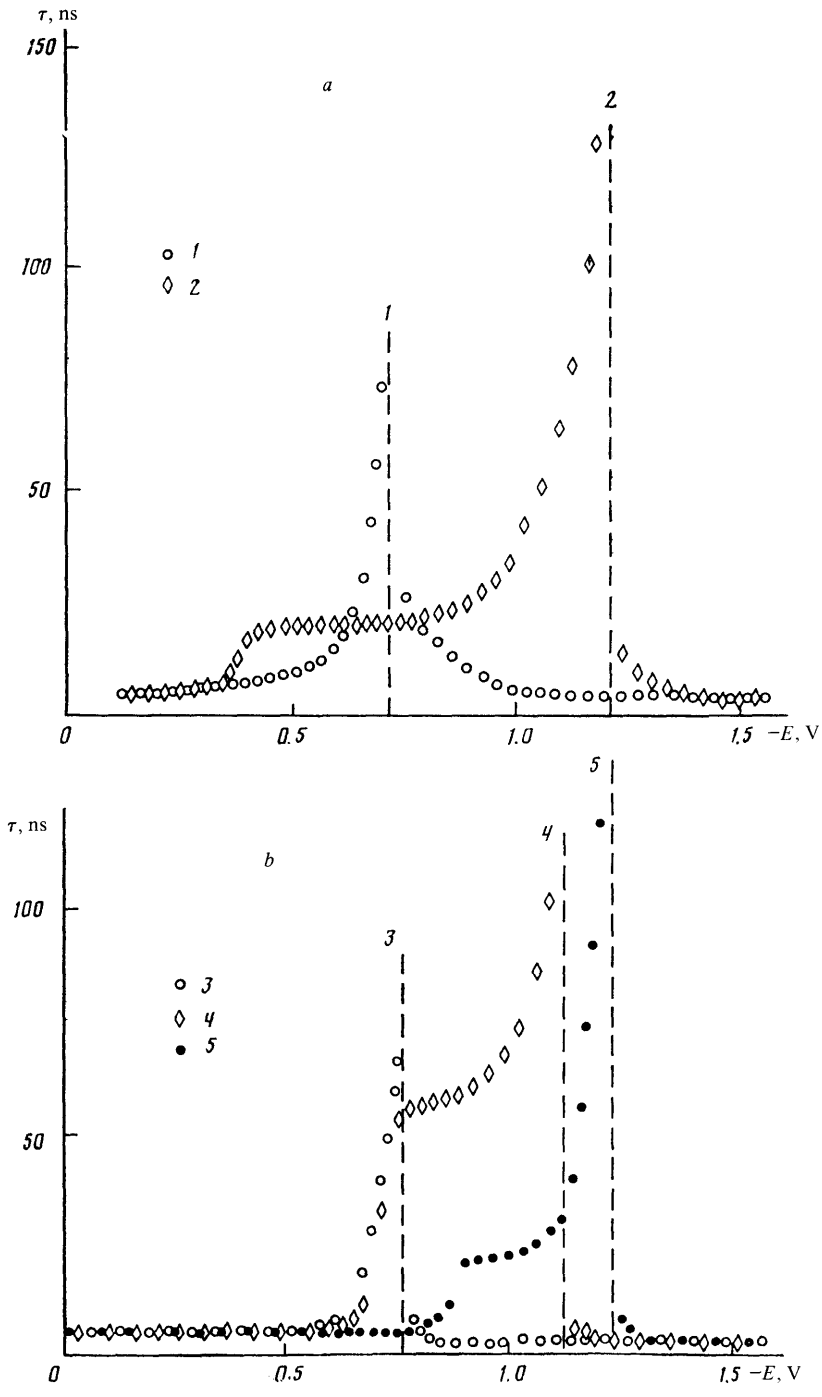


Figure 13. Characteristics EDL relaxation time for the adsorption of phenol (*a*) and 1,3,5-trihydroxybenzene (*b*) on mercury; the OS concentrations are 4×10^{-3}, 0.2, 10^{-3}, 4×10^{-2}, and 0.1 M for curves *1*–*5* respectively.[64]

Despite the limited number of examples of the application of the LTJ method, the data obtained show that the combination of the new method with the traditional procedures ensures a fairly complete thermodynamic description of the EDL both in terms of derivatives of the thermodynamic potential with respect to electrical variables and activities and in terms of temperature. The sharp changes in the relaxation times observed by the LTJ method in the regions of singularities in these derivatives display a set of different phase states of the EDL and the transitions between them of both first and second orders. Further development of this field will be associated

with the testing of structural models of two-dimensional phases and phase transitions, which can be achieved, in particular, with the aid of electroreflection spectra and IR and Raman spectroscopy. The version of LTJ developed is designed for the measurement of relaxation times within a comparatively narrow range $10^{-8}-10^{-6}$, which is known *a priori* not to include the entire relaxation spectrum of the EDL. The high thermal conductivities of metals and the possibility of changes in the duration of the laser pulses make it possible to extend the dynamic range of the LTJ (approximately to $10^{-10}-10^{-4}$ s), creating thereby the relaxation spectroscopy of the EDL.

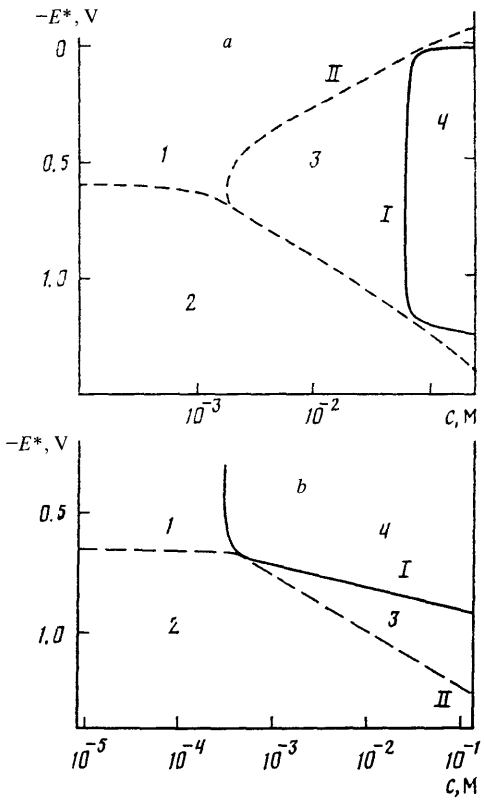


Figure 14. EDL phase diagrams for the adsorption of n-pentyl alcohol (*a*) and 1,3,5-trihydroxybenzene (*b*) on mercury; the continuous and dashed lines indicate the first- and second-order transitions respectively: 1) ice crystal; 2) OS solution in water; 3) mesophase; 4) mixed crystal of water and OS.[60,64]

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Institute of the Energetic
Problems of Chemical Physics,
USSR Academy of Sciences,
Moscow