ON THE ADSORPTION OF IONS ON MERCURY FROM CONCENTRATED AQUEOUS SOLUTIONS OF KCl AND CsCl

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The theory of the double layer developed by Grahame [1-4] makes it possible to determine the ionic components of the charge on an interfacial boundary. One of the basic postulates of this theory is the assumption that inorganic cations do not possess specific adsorbability and, consequently, in the presence of negative charges of the surface (ε), all the ions are found in the diffusion portion of the double layer. In this case, for a 1-1-valent electrolyte

$$F\Gamma_{\pm}^{\mathrm{el}} = \eta_{\pm}^{d} = \mp\frac{\varepsilon}{2} + \sqrt{\frac{DRTc}{2\pi} + \frac{\varepsilon^2}{4}} - \sqrt{\frac{DRTc}{2\pi}}, \tag{1}$$

where $\Gamma_{\pm}^{\mathrm{el}}$ is the adsorption of the cations or anions, due to electrostatic interaction; $\eta_{\pm}^{d}$ is the charge of the ions in the diffusion layer; D is the dielectric constant of water; c is the concentration of the electrolyte. According to equation (1), $\Gamma_{\pm}^{\mathrm{el}}$ increases with increasing negative value of ε and decreases as c increases, approaching a constant positive value equal to $|\varepsilon/2|$.

Grahame [1] noted coincidence of the values of $\Gamma_{\pm}$ at $\varepsilon < 0$, obtained from the electrocapillary curves in solutions of 0.3 and 1.0 N NaCl [5] and calculated according to Eq. (1). However, Grahame's postulate of the absence of any specific adsorption of inorganic cations contradicts their influence on the rate of reduction of a number of anions [6] and on the overvoltage of hydrogen [7]. The conclusion of superequivalent adsorption of the cations Cs^+ can also be drawn according to the data of a measurement of the differential capacitance C [8]. A study of the adsorption of ions from solutions of HCl, HBr, HI by the electrocapillary curve method showed [9] that as the acid concentration increases, Γ_+ decreases, while when $c > 10$ N and $\varepsilon < 0$, $\Gamma_+ < 0$, which patently contradicts Eq. (1). The derivation of Eq. (1) contains approximations permissible only in dilute solutions. The theory of the double layer in concentrated solutions was developed in [10].

The literature does not contain sufficient data on the measurement of the electrocapillary curves in concentrated solutions of neutral salts, with the exception of [11], from which it follows [12] that the values of Γ_+ in solutions of potassium salts lie below the corresponding data obtained by Grahame's method [2-4], the discrepancy increasing with increasing salt concentration. The different value of the adsorption obtained according to these two methods was explained in [4] by the fact that the surface excess relates to different planes of separation: in the electrocapillary-curve method – to the Gibbs planes, for which $\Gamma_{H_2O} = 0$, while in the capacitance method – to the outer Helmholtz plane. However, in [12], this discrepancy was related to the insufficient accuracy of the capacitance measurement. In view of the above, it was of interest to study the adsorption of ions in concentrated solutions of salts of the alkali metals by the electrocapillary-curve method.

A calculation of the adsorption of ions on the charged surface from the electrocapillary curves can be performed according to the Gibbs equation, which for the case of dilute solutions takes the form

$$\Gamma = \Gamma_+ + \Gamma_- = -\left(\frac{\partial\sigma}{\partial\mu}\right)_{\varphi}. \tag{2}$$

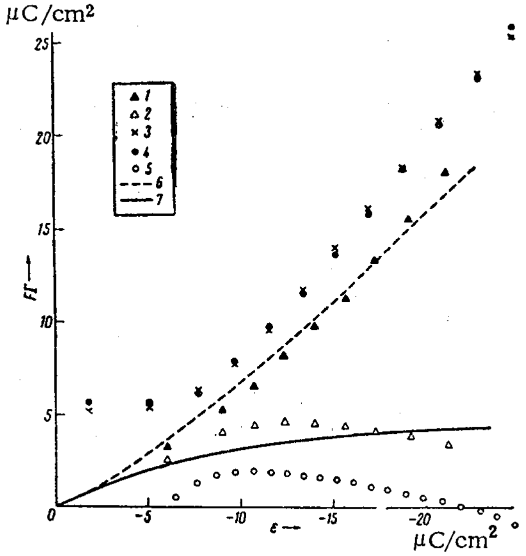

Fig. 1. Dependence of the adsorption of ions on the charge in 1 N solutions of KCl and CsCl: 1) $F\Gamma_{K^+}$ according to Eq. (4); 2) $(-F\Gamma_{Cl^-})$ according to Eq. (4) for a solution of KCl; 3) $F\Gamma_{Cs^+}$ according to Eq. (4); 4) $(F\Gamma_{Cs^+})$ according to Eqs. (2) and (3); 5) $(-F\Gamma_{Cl^-})$ according to Eqs. (2) and (3) for a solution of CsCl; 6) $F\Gamma_+^{el}$ according to Eq. (1); 7) $(-F\Gamma_-^{el})$ according to Eq. (1).

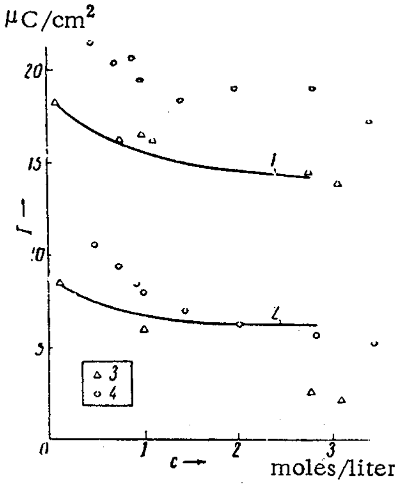

Fig. 3. Dependence of the adsorption of the cations K$^+$ and Cs$^+$ on the concentration: 1) $F\Gamma_+^{el}$ at $\varepsilon = -20$ μC/cm^2 according to Eq. (1); 2) $F\Gamma_+^{el}$ at $\varepsilon = -10$ μC/cm^2 according to Eq. (1); 3) $F\Gamma_{K^+}$ according to Eq. (4); 4) $F\Gamma_{Cs^+}$ according to Eq. (4).

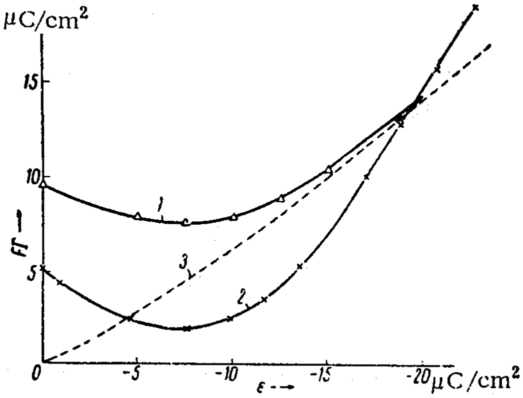

Fig. 2. Dependence of the adsorption of ions K$^+$ on the charge in 2.78 and 2.5 N Cl solutions: 1) Quantity η_+^d for 2.5 N KCl according to the data of [4]; 2) $F\Gamma_+$ according to Eq. (4); 3) $F\Gamma_+^{el}$ according to Eq. (1).

Equation (2), in conjunction with the Lippman equation

$$\left(\frac{\partial\sigma}{\partial\varphi}\right)_\mu = -\varepsilon = F(n_+\Gamma_+ - n_-\Gamma_-) \qquad (3)$$

makes it possible to determine Γ_+ and Γ_- individually. In these equations σ is the boundary tension; μ is the chemical potential of the electrolyte; φ is the electrode potential, measured with respect to a constant comparison electrode; $n_\pm$ is the valence of the cation and anion, respectively. Equation (2) cannot be extended to concentrated solutions in the case of a metal/solution interface. The latter is due to the fact that the very concept of constancy of φ with variation of the composition of the solution cannot be used in this case. The exact equation, derived in different ways in [14] and [9]:

$$\Gamma_\pm = -\left(\frac{\partial\sigma}{\partial\mu}\right)_{\varphi_\mp}, \qquad (4)$$

where $\varphi_\mp$ is the potential of mercury, measured with respect to an electrode submerged in this same solution, reversible with respect to the anion or cation, is suitable for calculating the value of the adsorption from solutions of any concentration. In the calculations according to Eq. (4), the interface is selected such that $\Gamma_{H_2O} = 0$.

Using the Gouy electrometer, we measured the electrocapillary curves for solutions of the salts KCl and CsCl of different concentrations. The reproducibility of the measurements was ± 0.2 dyne/cm. The maximum error in the determination of $F\Gamma_\pm$ was equal to ± 6 μC/cm^2. It was established that the calomel and silver chloride electrodes cannot be used at CsCl concentrations above 4 N, since an increase in the solution of Hg_2Cl_2 and AgCl is observed. For this reason, the measurements of the electrocapillary curves in solutions of CsCl were limited to the indicated concentration. The charge on the surface was determined by graphical integration of the C, φ curves, which were taken according to the procedure described in [15]. The integration constant was determined from the electro-

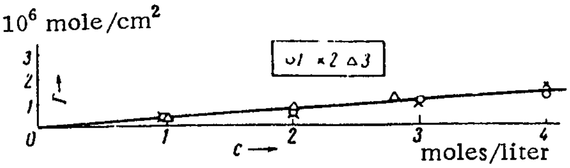

Fig. 4. Dependence of the negative adsorption of the salt at $\varphi_{\varepsilon = 0}$ on the concentration of the electrolyte in solutions: 1) $MnSO_4$; 2) K_2CO_3; 3) $MgSO_4$.

capillary curves in the corresponding solution according to the position of the electrocapillary maximum, found by the method of the mean diameter. The accuracy of the measurements was verified by comparing the values of ε, obtained in one case by differentiation of the σ, φ-curve, and in the other by integration of the C, φ curve. For a 4 N solution of CsCl, the difference in the values of ε obtained by the two methods did not exceed 0.3 $\mu C/cm^2$. The adsorption was calculated according to Eq. (4), and for dilute solutions also according to Eqs. (2) and (3), which served as a check on the reliability of the experimental data. The activity coefficients were taken from [16].

The results obtained are presented in Figs. 1-3. As can be seen from Fig. 1, in 1 N KCl, when $\varepsilon < 0$, the value of the adsorption of the cation K^+ practically coincides with η_+^d. Consequently, the K^+ ion does not exhibit specific adsorbability, possibly with the exception of the extreme cathode polarizations. As the concentration increases, the general negative adsorption of the salt is superimposed upon the electrostatic adsorption [9], and Γ_+ decreases in the region of ε from -5 to -20 $\mu C/cm^2$ (see curve 2 in Fig. 2). This result is in good agreement with the data of [9]. From Fig. 2 (curve 1), it follows that in calculation according to the capacitance method of Grahame [4], we do not ascertain the decrease in the adsorption of the cations K^+.* The authors of [4] explained such a difference in the results of the two methods by the "concentration factor," which arises when the Gibbs plane is displaced by a distance x (from the plane $\Gamma_{H_2O} = 0$ to the outer Helmholtz plane). We evaluated x according to the equation

$$\eta_+^d - \Gamma_+ = xc \tag{5}$$

(see [4]). Thus, for KCl when $\varepsilon = -10$ $\mu C/cm^2$, x = 2.33 A, and when $\varepsilon = -15$ $\mu C/cm^2$, x = 1.14 A, from which it follows that x varies with the charge of the surface. The dependence of x on ε leads to the conclusion that Grahame's theory cannot be applied for quantitative calculations in concentrated solutions, even in the absence of specific adsorption of the cations.

The results obtained are also of interest because the question of the thickness of the interlayer of solvent between the ions of the double layer and surface of the electrode has recently been repeatedly discussed from various viewpoints [17, 18]. We performed a calculation of the negative adsorption of the salt (Γ_{salt}) at the potential of the maximum of the electrocapillary curves for capillary-inactive salts according to the equation

$$\Gamma_{salt} = -\frac{1}{\nu RT}\left(\frac{\partial\tau}{\partial \ln a_\pm}\right), \tag{6}$$

where ν is the sum of the number of cations and anions formed in the dissociation of a salt molecule and $a_\pm$ is the average activity of the ions of the electrolyte. The values of σ were taken from the data of Gouy [5]; the values of $\alpha_\pm$ for $MnSO_4$ and $MgSO_4$ – from [16], and for K_2CO_3 – from [19]. The slope of the dependence of Γ_{salt} on c (Fig. 4) determines the quantity x. The average value of x in solutions of $MnSO_4$, $MgSO_4$ and K_2CO_3 is equal to 3.3 A, which gives evidence of the possibility of introduction of only one molecule of water into the space between the surface of the electrode and the outer Helmholtz plane.

From Figs. 1 and 3 it is evident that, in agreement with the indirect data [6-8], the Cs^+ ion exhibits specific adsorbability. When the CsCl concentration increases, the effect of the general negative adsorption leads to a decrease in the specific adsorption of Cs^+, and hence the latter passes through a maximum, corresponding to an ~0.5 N solution of CsCl, in which even an overcharging of the surface of the electrode by Cs^+ ions is observed. Thus, in solutions of cesium salts, Grahame's theory is inapplicable at low concentrations.

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*The values of the components of the charge of the double layer in solutions of KCl, obtained by the capacitance method [4], were kindly provided us by Dr. P. Parsons, to whom we should like to express our profound gratitude.

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