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Abstract

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

Grahame’ s theory of the double layer ($^{1-4}$) makes it possible to determine the ionic components of the charge at the interphase boundary. One of the basic postulates of this theory is the assumption that inorganic cations do not possess specific adsorbability and, consequently, at negative surface charges (ε) all ions are located in the diffuse part of the double layer. In this case, for a 1–1-valent electrolyte,

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

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

Grahame (^{1}) noted agreement of the values of $\Gamma_{\pm}$ at $\varepsilon < 0$, obtained from electrocapillary curves (e.c.c.) in 0.3 and 1.0 N NaCl solutions (^{5}), with those calculated from equation (1). However, Grahame’ s postulate on the absence of specific adsorption of inorganic cations is in contradiction with their influence on the rate of reduction of a number of anions (^{6}) and on the hydrogen overvoltage (^{7}). A conclusion about super-equivalent adsorption of Cs^{+} cations could also be drawn from measurements of the differential capacitance C (^{8}). A study of ion adsorption from HCl, HBr, and HI solutions by the e.c.c. method showed (^{9}) that with increasing acid concentration Γ_{+} decreases, and at $c > 10$ N and $\varepsilon < 0$, $\Gamma_{+} < 0$, which plainly contradicts equation (1). The derivation of equation (1) contains approximations permissible only in dilute solutions. The theory of the double layer in concentrated solutions was developed in (^{10}).

There are not enough data in the literature on measurements of e.c.c. in concentrated solutions of neutral salts, with the exception of work (^{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 ($^{2-4}$), and the discrepancy

Figure 1

Figure 1: Figure 1

increases with increasing salt concentration. The different value of the adsorption obtained by these two methods was explained in (4) by the fact that the surface excess refers to different planes of division: in the e.c.c. method—to the Gibbs plane, for which $\Gamma_{H_2O} = 0$, and in the capacitance method—to the outer Helmholtz plane. However, in (12) this discrepancy was attributed to insufficient accuracy of capacitance measurement. In connection with the foregoing, it was of interest to study the adsorption of ions in concentrated solutions of alkali-metal salts by the e.c.c. method.

The calculation of ion adsorption on a charged surface from e.c.c. can be carried out according to the Gibbs equation, which for the case of dilute solutions has the form

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

Equation (2), in combination with the Lippmann equation

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

makes it possible to determine Γ_{+} and Γ_{-} separately. In these equations σ is the interfacial tension; μ is the chemical potential of the electrolyte; φ is the electrode potential measured with respect to a constant reference electrode; $n_{\pm}$ are the valences of the cation and anion, respectively. Equation (2) cannot be extended to concentrated solutions in the case of the metal/solution boundary. The latter is connected with the fact that the very concept of the constancy of φ when the composition of the solution changes cannot be used in this case (13). For calculating the adsorption from solutions of any concentration, the exact equation derived in different ways in (14) and (9) is suitable:

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

where $\varphi_{\pm}$ is the potential of mercury measured relative to an electrode immersed in the same solution and reversible with respect to the anion or cation. In calculations by equation (4), the dividing surface is chosen so that $\Gamma_{H_2O} = 0$.

Fig. 1. Dependence of ion adsorption on charge in 1 N KCl and CsCl solutions: 1 $-F\Gamma_{K^+}$ according to equation (4); 2 $-(-F\Gamma_{Cl^-})$ according to equation (4) for a KCl solution; 3 $-F\Gamma_{Cs^+}$ according to equation (4); 4 $-(F\Gamma_{Cs^+})$ according

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

to equations (2) and (3); 5 $-(-F\Gamma_{\mathrm{Cl}^-})$ according to equations (2) and (3) for a CsCl solution; 6 $-F\Gamma_+^{\mathrm{el}}$ according to equation (1); 7 $-(-F\Gamma_-^{\mathrm{el}})$ according to equation (1).

Using a Gouy electrometer, we measured the emf for solutions of KCl and CsCl salts of various concentrations. The reproducibility of the measurements was ±0.2 dyn/cm. The maximum error in determining $F\Gamma_\pm$ was $\pm 0.6\,\mu\mathrm{C/cm^2}$. It was established that calomel and silver chloride electrodes cannot be used at CsCl concentrations above 4 N, since an increase in the dissolution of $\mathrm{Hg_2Cl_2}$ and AgCl is observed. For this reason, emf measurements in CsCl solutions were limited to the indicated concentration. The surface charge was determined by graphical integration of C, φ-curves, which were recorded by the procedure described in $^{(15)}$. The integration constant was determined from the emf in the corresponding solution by the position of the electrocapillary maximum, found by the mean-diameter method. The accuracy of the measurements was checked by comparing the values of ε obtained in one case by differentiating the σ, φ-curve and in the other by integrating the C, φ-curve. For a 4 N CsCl solution, the difference in the value of ε obtained by the two methods did not exceed $0.3\,\mu\mathrm{C/cm^2}$. The adsorption was calculated by equation (4), and for dilute solutions also by equations (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 at $\varepsilon < 0$ the adsorption of the cation K^+ practically coincides with η_+. Consequently, the K^+ ion does not exhibit specific adsorbability, possibly with the exception of the extreme cathodic polarizations. As the concentration increases, electrostatic adsorption is superimposed by

the total negative adsorption of the salt (^{9}), and Γ_+ decreases in the region of ε from -5 to -20 $\mu\mathrm{C/cm^2}$ (see curve 2 in Fig. 2). This result agrees well with the data of (^{9}). It follows from Fig. 2 (curve 1) that, when calculated by the capacitance method of Grahame (^{4}), we do not observe a decrease in the adsorption of K^+ cations*. The authors of (^{4}) explained this difference in the results of the two methods by a

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

Fig. 3. Dependence of the adsorption of K^+ and Cs^+ cations on concentration: 1–$F\Gamma_+^{\mathrm{el}}$ at $\varepsilon = -20$ $\mu\mathrm{C/cm^2}$ according to equation (1); 2–$F\Gamma^{\mathrm{el}}$ at $\varepsilon = -10$ $\mu\mathrm{C/cm^2}$ according to equation (1); 3–$F\Gamma_{K^+}$ according to equa-

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

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

tion (4); 4—$F\Gamma_{Cs^+}$ according to equation (4)

"concentration factor," which arises when the Gibbs plane is displaced by a distance x (from the plane $\Gamma_{\mathrm{H_2O}} = 0$ to the outer Helmholtz plane). According to the equation

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

(see ([4])) we estimated the value of x. Thus, for KCl at $\varepsilon = -10$ μC/cm^2, $x = 2.33$ Å, and at $\varepsilon = -15$ μC/cm^2, $x = 1.14$ Å, from which it follows that x changes with the surface charge. 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 cations.

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

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

where ν is the sum of the numbers of cations and anions formed upon dissociation of the salt molecule, and $a_\pm$ is the mean activity of the electrolyte ions. The values of σ were taken from the data of Gouy ([5]); the values of $a_\pm$ 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 value of x. The mean value of x in solutions of $MnSO_4$, $MgSO_4$, and K_2CO_3 is equal to 3.3 Å, which indicates the possibility of penetration of only one water molecule into the space between the electrode surface and the outer Helmholtz plane.

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

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

From Figs. 1 and 3 it is seen that, in agreement with indirect data ($^{6-8}$), the Cs^+ ion exhibits specific adsorbability. With increasing CsCl concentration, the effect of general negative adsorption leads to a decrease in the specific adsorption of Cs^+, and therefore the latter passes through a maximum corresponding to ~ 0.5 N CsCl solution, in which even a reversal of the charge of the electrode surface by Cs^+ ions is observed. Thus, in solutions of cesium salts, Grahame' s theory is inapplicable at low concentrations.

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