A MIXED-ELECTROLYTE STUDY OF CESIUM-ION ADSORPTION FROM AQUEOUS SOLUTIONS ONTO MERCURY

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In [1] we have used the Hurwitz – Parsons method [2,3] with the systems NaCl + CsCl and Na_2SO_4 + Cs_2SO_4 in water to study the adsorption of cesium ions on a negatively charged mercury surface ($\varepsilon < 0$). It was found that the charge density of specifically adsorbed cesium ions (ε_1) is highly significant, even though it does not lead to charge reversal of the mercury surface, i.e., $|\varepsilon_1| < |\varepsilon|$. It had been shown in [4] that in the mixed-electrolyte method, the surface activity of the reference ion appreciably distorts the ε_1 value being determined. That there is some specific adsorption of sodium ions can be concluded from measured differential-capacitance data [5], because there is an increase in capacitance in solutions of like concentrations at negative electrode charge which follows the order LiCl < NaCl < KCl < CsCl. The data on the specific adsorption of cesium obtained in [1] could, therefore, be expected to be somewhat too low, owing to the effect of specific adsorption of the reference ions.

Parsons and Stockton's data [6] for the system xN CsCl + (1 − x) N LiCl are free from this defect, but owing to the high total electrolyte concentration, double-layer parameter calculations based on the Gouy – Chapman theory become ill-founded for this system. The results for this system can, on the other hand, be distorted because of joint adsorption of Cs^+ and Cl^- ions. It was appropriate, therefore, to study the adsorption of cesium ions from aqueous solutions onto mercury in the system CsCl + LiCl at lower ionic strength (J) of the solution.

It was of interest at the same time to elucidate the effect of ionic strength of the solution on the value to be determined for the specific adsorption of cesium ions. Two systems were studied in the present work: I, xN CsCl + (0.1 − x) N LiCl, and II, xN CsCl + (0.01 − x) N LiCl. Any error committed in determining the magnitude of specific adsorption of the ions can be neglected. Using an R-568-type impedance bridge we have recorded for systems I and II the differential capacitance (C) as function of potential (φ) of a dropping mercury electrode for different values of x. The surface charge density ε was determined by numerical integration of the C − φ curves. The potentials of zero charge for the LiCl solutions were taken from [7]; in the case of mixed solutions, it was assumed that φ_{zc} is independent of x.

Curves showing the dependence of electric double-layer capacitance on electrode charge density are shown in Fig. 1. An interesting feature of the capacitance curves is the lack of dependence of the quantity $\Delta C = C_{Cs^+} - C_{Li^+}$ on the ionic strength of the solution at ε = const. One can propose on the basis of this result that the extent of specific adsorption of cesium is independent of the ionic strength J of the solution while this changes from 0.01 to 0.1 mole/liter.

TABLE 1

c, mole/liter	K_{∞}, μF/cm²	K_{12}, μF/cm²	$(x_2 - x_1)/x_2$
0,01	15,1	88	0,17
0.1	15,6	76	0,20

The specific adsorption of the cesium ions at different ε has been determined by graphical differentiation of the $\Delta\xi - \log x$ curves using the equation [3]

$$\varepsilon_1 = \frac{F}{RT}\left(\frac{\partial \Delta\xi}{\partial \ln x}\right)_{\varepsilon}. \qquad (1)$$

The use of this equation is justified because, within the concentration range indicated, the system selected obeys the Harned rule [8], in agreement with a requirement of the mixed-

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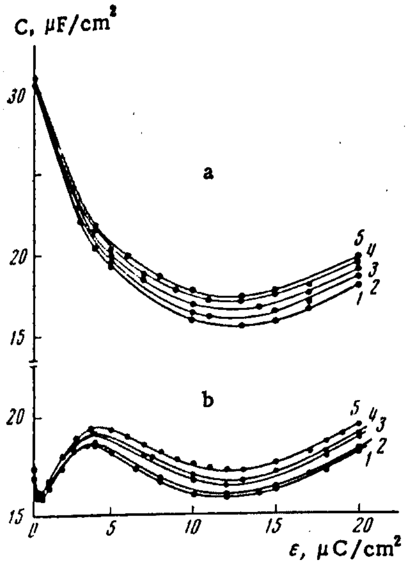

Fig. 1. Capacitance of the electric double layer as function of electrode charge density. a) For the system xN CsCl + (0.1 − x) N LiCl: 1) x = 0; 2) x = 5 · 10⁻³; 3) x = 2 · 10⁻²; 4) x = 5 · 10⁻²; 5) x = 0.1; b) for the system xN CsCl + (0.01 − x) N LiCl: 1) x = 0; 2) x = 2 · 10⁻⁴; 3) x = 1 · 10⁻³; 4) x = 2 · 10⁻³; 5) x = 0.01.

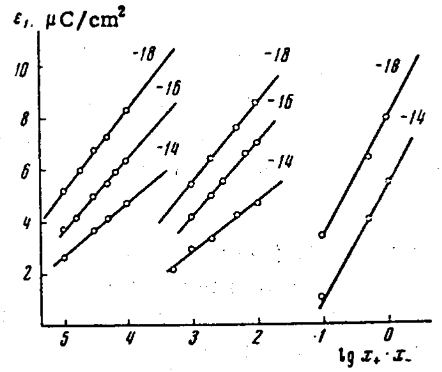

Fig. 2. Charge density of specifically adsorbed Cs$^+$ ions as function of the logarithm of salt activity in the solution. The numbers at the curves indicate the charge density of the mercury electrode in μC/cm^2.

electrolyte method [2]. The values for the two-dimensional pressure of the specifically adsorbed ions, $\Delta\xi$, were obtained with the aid of the following relations:

$$\Delta\frac{1}{C}=\frac{1}{C_{\mathrm{Li^+}}}-\frac{1}{C};\quad \Delta\varphi=\int\limits_{\varepsilon(\Delta(1/C)=0)}^{\varepsilon}\Delta\frac{1}{C}\,d\varepsilon;\quad \Delta\xi=\int\limits_{\varepsilon(\Delta\varphi=0)}^{\varepsilon}\Delta\varphi\,d\varepsilon, \tag{2}$$

where $\Delta\varphi$ is the potential shift produced by the active additive in the solution. On the basis of the values of specific adsorption of cesium ions thus obtained and using the scheme of calculations proposed by Grahame and Parsons [9], we have calculated the following parameters of the electric double layer for the systems studied: the charge density of the diffuse layer ε_2, the potential of the outer Helmholtz plane ψ^0, the potential drop across the compact part of the double layer ψ^u, the integral capacitances of the compact layer K_{12} and K_{02} measured at ε = const and ε_1 = const, respectively, and the ratio $(x_2 - x_1)/x_2$, where x_1 and x_2 are the distances of separation of the inner and outer Helmholtz plane from the electrode surface. The averaged values of K_{02}, K_{12}, and $(x_2 - x_1)/x_2$ are given in Table 1.

It should be noted that the ratio $(x_2 - x_1)/x_2$ for the systems being studied is in good agreement with the analogous value of 0.174 found previously by us for the system CsCl + NaCl [1].

Figure 2 shows the charge density of specific adsorption of cesium ions as function of the logarithm of salt activity in the solution at a few electrode charge densities. The data of Parsons for the system xN CsCl + (1 − x) N LiCl [6] are also shown there. It can be seen from this figure that the specific adsorption of cesium is practically independent of the ionic strength of the solution, and is only determined by the proportion of surface-active component in the solution. With m = 1 this means that it has no effect upon the value of ε_1 when the CsCl concentration is raised by two orders of magnitude (from 0.01 to 1).

Figure 3 shows the potential of the outer Helmholtz plane for the ε_1 values found (at x = 0.1 and x = 0.01) and for the condition $\varepsilon_1 = 0$. It is an interesting conclusion to be drawn from this figure that the change in ψ^0 potential which occurs when going from the salt LiCl to the salt CsCl is practically independent of the ionic strength of the solution. One can say that this is the result of ε_1 being independent of ionic strength of the solution. Actually, according to diffuse-layer theory for a 1:1 electrolyte, the potential of the outer Helmholtz plane is

$$\psi_0=\frac{2RT}{F}\operatorname{arcsh}\left(\frac{\varepsilon+\varepsilon_1}{2A\sqrt{c}}\right)=\frac{2RT}{F}\ln\left[\sqrt{1+\frac{(\varepsilon+\varepsilon_1)^2}{4A^2c}}+\frac{\varepsilon+\varepsilon_1}{2A\sqrt{c}}\right]=-\frac{2RT}{F}\ln\left[\sqrt{1+\frac{(\varepsilon+\varepsilon_1)^2}{4A^2c}}-\frac{\varepsilon+\varepsilon_1}{2A\sqrt{c}}\right], \tag{3}$$

where $A=\sqrt{DRT/2\pi}$. When $|\varepsilon_1| < \varepsilon$, which is true in our case, and under the condition $(\varepsilon_1+\varepsilon)^2 \gg 4A^2c$,

$$\psi_0\approx-\frac{RT}{F}\ln\frac{(\varepsilon+\varepsilon_1)^2}{A^2}+\frac{RT}{F}\ln c. \tag{4}$$

In the absence of specific adsorption, under the condition $\varepsilon^2 \gg 4A^2c$,

$$\psi_0^{(\varepsilon_1=0)}\approx-\frac{RT}{F}\ln\frac{\varepsilon^2}{A^2}+\frac{RT}{F}\ln c.$$

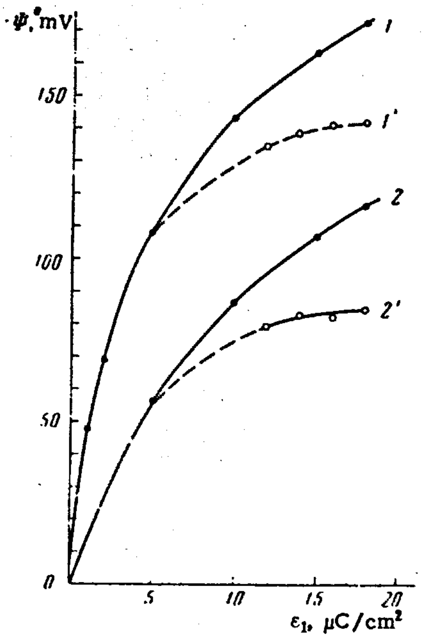

Fig. 3. Potential of the outer Helmholtz plane as function of surface charge density in the system: mc CsCl + (1 − m) · c LiCl: 1) c = 0.1; 2) c = 0.01 M; 1, 2) for the case $\varepsilon_1 = 0$; 1', 2') for $\varepsilon_1 \neq 0$.

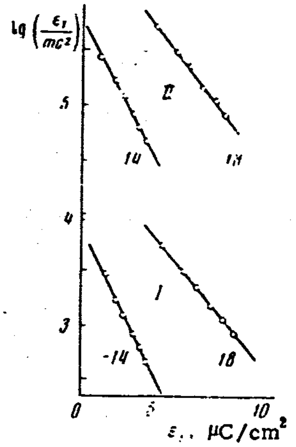

Fig. 4. The quantity log (ε_1/mc^2) as function of the charge density of cations specifically adsorbed on the mercury; the plots were constructed from the experimental ε_1 values according to Eq. (3); I) c = 0.1; II) c = 0.01 M. Numbers at the straight lines indicate ε in μC/cm².

Therefore, the change in the potential of the outer Helmholtz plane when going from $\varepsilon_1 = 0$ to some finite value of specific adsorption will be

$$\Delta\psi^0 = \psi_0^{(\varepsilon_1=0)} - \psi_0 = \frac{RT}{F}\ln\frac{(\varepsilon+\varepsilon_1)^2}{A^2} - \frac{RT}{F}\ln\frac{\varepsilon^2}{A^2} = \frac{RT}{F}\ln\frac{(\varepsilon+\varepsilon_1)^2}{\varepsilon^2}, \quad (5)$$

i.e., the quantity $\Delta\psi^0$ is independent of the ionic strength of the solution, as observed experimentally (see Fig. 3). It appears that this should be taken into account when interpreting the effect of the electric double layer on the kinetics of electrode reactions.

A virial isotherm of the form [10]

$$\ln(\beta_B c_+ c_-) = \ln\varepsilon_1 + 2B\varepsilon_1, \quad (6)$$

was used by us to determine the adsorption equilibrium constant, the adsorption energy, and the coefficient of repulsive interaction; here β_B is the adsorption equilibrium constant, and B is the second virial coefficient. Figure 4 shows the dependence of $F_1 = \log(\varepsilon_1/mc^2)$ on ε_1 for systems I and II and $\varepsilon = -14$ and $-18\ \mu C/cm^2$. It follows from this figure that the specific adsorption can be described by Eq. (6), but for a given electrode charge density, the plots of F_1 against ε_1 for c = 0.1 and 0.01 deviate by about two from one another. Therefore, the values of the adsorption equilibrium constant, which characterize the free energy of adsorption, will also differ by two orders of magnitude. On the other hand, at m = 1 we already have a pure CsCl solution, where the parameter describing the free energy of the given ion must not depend on salt concentration. This leads to the general conclusion that the simple virial isotherm (6) cannot be used to obtain the free energy of adsorption of a given ion, because this isotherm takes no account of the diffuse electric double layer.

We have shown previously [11] that it follows from the equations of diffuse-layer theory that under the condition $|\varepsilon_1| < \varepsilon$, the specific adsorption of a cation is practically without any effect on the total surface excess. In other words, the surface excess remains practically constant while the specific adsorption of the ions varies, e.g., from 0 to 15 μC/cm² for a 0.1 N solution. Both effects (independence of the specific adsorption of an ion on the total ionic strength of the solution, and independence of the total surface excess on the magnitude of specific adsorption at a given ionic strength) are due to buffering action of the diffuse double layer in the specific adsorption of ions. A separate communication will deal with a qualitative interpretation of this effect.

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