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Academician A. N. FRUMKIN, B. B. DAMASKIN, and N. V. NIKOLAEVA-FEDOROVICH

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Abstract

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Academician A. N. FRUMKIN, B. B. DAMASKIN, and N. V. NIKOLAEVA-FEDOROVICH

SUPEREQUIVALENT ADSORPTION OF CATIONS ON A NEGATIVELY CHARGED MERCURY SURFACE

Usually, in presenting the theory of electrocapillarity it is assumed that, among inorganic ions, only anions possess specific adsorbability, while the concentration of inorganic cations in the electrical double layer is determined solely by the magnitude of their charges ([1]). However, there are data in the literature indicating the inaccuracy of such a conclusion. Thus, for example, in the work of L. M. Stifman a certain superequivalent adsorption of the aluminum cation was found ([2]).

A direct conclusion about the different adsorbability of alkali-metal cations in $0.1\,N$ chloride solutions follows from the work of D. Grahame, who determined precise values of the differential capacitance in these solutions ([3]). Indeed, at potentials more negative than -0.7 V (against $0.1\,N$ c.e.), an increase in capacitance is observed on going from lithium to cesium, and, consequently, an increase in the surface charge as well. However, according to D. Grahame, the difference in surface charge found by comparing the differential capacitances is entirely reduced to the difference in the capacitance of the Helmholtz part of the double layer*. With such an interpretation of D. Grahame' s experimental data, a larger negative charge should correspond to a more negative value of the ψ_1-potential ([5]). This conclusion is in poor agreement with experimental data on the influence of the radius of the background cation on the rate of reduction of anions. It turns out that the rate of reduction of the anions $S_2O_8^{--}$ ([6]) and $S_4O_6^{--}$ ([7]) increases sharply in the series
$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, i.e., a dependence of the rate of the process is observed that is the reverse of that which would naturally be expected in accordance with D. Grahame' s conclusion. A more detailed discussion of this question is given in the work of A. N. Frumkin and N. V. Nikolaeva-Fedorovich ([5]).

To avoid contradiction in explaining the experimental data, it is simplest to assume a certain, albeit small, specific adsorption of cations with larger radius.

Figure 1

Figure 1: Figure 1

The study of the temperature coefficient of the electroreduction reaction of anions leads to the same conclusion. Thus, in the case of reduction of $S_2O_8^{--}$ against a background of 0.01 *N* NaCl, the temperature coefficient of this reaction has a small positive value; against a background of potassium cation of the same concentration it is practically zero, while against a background of cesium cation the temperature coefficient has a negative value ([5],[8]).

To test the assumption of the presence of specific adsorption of cations, measurements of the differential capacitance were carried out in 0.01 *N* solutions of alkali-metal chlorides. The impedance-bridge arrangement used for the measurements did not differ in principle from the arrangements described in the works of D. Grahame ([9]) and V. I. Melik-Gaikazyan ([10]). The electrode under investigation was a hanging mercury drop.

* In one of his papers D. Grahame indicates that, for explaining the experimental data on adsorption of the Cs^+ cation, this assumption is possibly insufficient ([4]).

The data obtained are presented in Fig. 1A, which shows differential-capacitance curves taken in 0.01 N solutions of lithium, potassium, and cesium chlorides. As can be seen from the figure, the difference in differential capacitance for cations with different radii is observed here not only at considerable negative potentials, but also near the point of zero charge, where the capacitance curves have a minimum. Indeed, on going from lithium to cesium, the difference in the capacitance values near

Fig. 1. Differential-capacitance curves. A—in 0.01 N solutions of CsCl (1), KCl (2), and LiCl (3); frequency 400 cps; 25°. B—in 0.1 N solutions of NaCl (1), NaJ (2), CsCl (3), and CsJ (4); frequency 1000 cps; 25°.

the point of zero charge is 1 $\mu F/cm^2$. The difference in the capacitance values of the electric double layer in solutions of lithium and cesium chlorides is an additional indication of the presence of specific adsorption of the cesium cation. However, this conclusion cannot be regarded as unambiguous, since the experimental data obtained in solutions of alkali-metal chlorides are complicated by adsorption of Cl^-. We intend in the near future to carry out capacitance measurements in solutions of sodium and cesium fluoride salts.

The most convincing data indicating the presence of superequivalent adsorption of cations can be obtained by measuring the differential capacitance on a negatively charged electrode surface in the presence of an anion such as J^-, whose adsorption in the surface layer has a noticeable effect on the magnitude of the differential capacitance.

We carried out measurements of the differential capacitance in 0.1 *N* solutions

Figure 2

Figure 2: Figure 2

of NaCl, NaJ, CsCl and CsJ, and also in solutions of 1.1 N KCl, 1N KJ +0.1N KCl, 1N KCl +0.1N $LaCl_3$, 1N KJ +0.1N $LaCl_3$. The results obtained are given in Figs. 1B and 2A. As is evident from the data presented, at sufficiently negative polarizations the iodide anion ceases to exert an influence, and the values of the differential capacitance for the corresponding chlorides and iodides converge. At more negative potentials the capacitance values are determined only by the cations present in the solution. However, the potentials at which the difference between the capacitance values for the corresponding chlorides and iodides disappears are not the same and depend on the nature of the cation. Thus, the action of iodine in the case of NaCl and NaJ solutions is manifested up to the potential $\varphi = -1.2$ V (against the n.c.e.), while in the case of CsCl and CsJ solutions up to the potential $\varphi = -1.3$ V (against the n.c.e.), which indicates a certain superequivalent adsorption of the Cs^+ cation, absent in the case of the Na^+ cation. An analogous effect is also observed upon addition to 1N KCl and KJ solutions of a 0.1 N $LaCl_3$ solution. Thus, the action of the J^- ion, which in a solution of 1.1 N KCl and 1N KJ +0.1N KCl is manifested up to the potential $\varphi = -1.55$ V (against the n.c.e.), in solutions of 1N KCl +0.1N $LaCl_3$ and 1N KJ +

Fig. 2. Curves of differential capacitance. **A** –in solutions of 1.1 N KCl (1), 1N KJ +0.1N KCl (2), 1N KCl +0.1N $LaCl_3$ (3), 1N KJ +0.1N $LaCl_3$ (4), frequency 1000 cps; 25°; **B** –in solutions of $10^{-3}N$ $[N(C_4H_9)_4]_2SO_4$ in the presence of 1N KCl (1), 1N KBr (2) and 1N KJ (3); frequency 1000 cps; 25°

+0.1N $LaCl_3$ persists down to a potential $\varphi = -1.65$ V (against the N.C.E.), indicating a certain superequivalent adsorption of the La^{+++} cation. The indicated phenomena can also be interpreted by assuming the presence in the electrical double layer of ionic pairs, for example, in the case of lanthanum, LaJ^{++} and $LaCl^{++}$, with the adsorbability of these complexes being greater in the former case than in the latter. As is seen from Figs. 1B and 2A, the sharp increase in capacitance associated with the introduction of anions into the electrical double layer is observed in the presence of Cs^+ or La^{+++} at more negative potentials than in solutions containing Na^+ or K^+. In other words, in this region of potentials the adsorption of J^- is facilitated by the presence in the surface layer of Cs^+ or La^{+++} ions, which, probably, are more readily adsorbed on the surface of mercury recharged by J^- ions than are Na^+ and K^+ ions.

L. M. Shtifman (2) also came to the conclusion, from electrocapillary measurements, that iodine anions are drawn into the double layer in the presence of Al^{+++} cations. Similar results were obtained by us in studying the boundary tension of Hg in solutions of 1N KCl +0.1N $LaCl_3$ and 1N KJ +0.1N $LaCl_3$, but these data require additional verification.

The fact that superequivalent adsorption of cations can lead to the entry of anions into the surface layer even at negative potentials is especially clearly manifested in the case of adsorption of organic cations. One of us (11) long ago arrived at this conclusion on the basis of electrocapillary measurements in solutions of $[N(C_3H_7)_4]Cl$, $[N(C_3H_7)_4]J$, and NH_4J. This phenomenon is also observed in measurements of the capacitance of a mercury electrode with the simultaneous presence in the solution of a surface-active organic cation and inorganic anions. At sufficiently negative potentials the cation $[N(C_4H_9)_4]^+$ is desorbed from the mercury surface with the formation on the differential-capacitance curve of a characteristic desorption peak (12).

Figure 2B presents data on the dependence of differential capacitance on potential in $1N$ solutions of KCl, KBr, and KJ in the presence of $10^{-3}N$ $[N(C_4H_9)_4]_2SO_4$. As is seen in the figure, the form of the desorption peak changes substantially on going from Cl^- to J^-. The noticeable sharpening of the peak indicates that instead of desorption over a narrow interval of potentials, there is observed a stepwise destruction of the adsorption layer at a quite definite potential ($\varphi = -1.57$ V against the N.C.E.). The dependence of the desorption process on the nature of the anion unambiguously indicates the drawing of anions into the surface layer at negative charges of the mercury surface. The approach of the anion to the negatively charged surface is facilitated by adsorbed cations, which are part of the double-layer plate facing the solution.

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