Physical Chemistry

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

1958

SovietRxiv

Abstract

Full Text

Physical Chemistry

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

ON THE ADSORPTION OF THE Cs^+ ION ON THE SURFACE OF A MERCURY ELECTRODE

In our previous work (^{1}) it was shown that on the negatively charged surface of a mercury electrode there is super-equivalent adsorption of the cations Cs^+ and La^{3+}. As evidence for this, the difference in the values of the differential capacitance at the point of zero charge (p.z.c.) on going from Li^+ to Cs^+ in $0.01\,N$ solutions of the chlorides of these metals was cited, as well as the difference between the potentials at which the difference disappears in the capacitance values for the corresponding $0.1\,N$ solutions of NaCl—NaJ and CsCl—CsJ. However, as has already been pointed out, these experimental data are complicated by the specific adsorption of the anions Cl^- and J^-, which affects the adsorption of cations on the surface of a mercury electrode. In order to avoid complications in the investigation of the super-equivalent adsorption of cations associated with the specific adsorption of anions, we carried out measurements in solutions of sodium and cesium fluorides, since, according to the data of D. Grahame (^{2,3}), the anion F^- is not specifically adsorbed on mercury.

The measurements were carried out by us with the aid of an impedance bridge, the circuit of which did not differ in principle from the circuits described in the works of D. Grahame (^{4}) and V. I. Melik-Gaikazyan (^{5}). The potentials of the electrodes are given in the work in volts against the normal calomel electrode. The cesium fluoride used in the work was obtained in the following way. By decomposing cesium amalgam in a fluoroplastic vessel, cesium hydroxide was prepared, which was then neutralized with hydrofluoric acid twice distilled in a palladium apparatus. The resulting solution was cathodically depolarized over mercury in a fluoroplastic vessel, and then, after evaporation, the CsF was ignited in a platinum crucible. We also used a commercial preparation of cesium fluoride, to which, in order to remove the CO_3^{2-} ion, twice-distilled hydrofluoric acid was added; it was likewise depolarized in a fluoroplastic vessel and ignited in a platinum crucible. Under these conditions both preparations gave identical results.

We measured the values of the differential capacitance on a mercury electrode in the form of a hanging drop in solutions of NaF and CsF of the following concentrations: 0.9, 0.1, and $0.01\,N$, and also in 0.9 and $0.1\,N$ solutions of

Fig. 1. Curves of differential capacitance in 0.9 N solutions: 1 –CsF, 2 –NaF, 3 –CsJ, 4 –NaJ. 1000 Hz. 25$±$0.1°

Figure 1: Fig. 1. Curves of differential capacitance in 0.9 N solutions: 1 –CsF, 2 –NaF, 3 –CsJ, 4 –NaJ. 1000 Hz. 25$±$0.1°

Fig. 2. Curves of differential capacitance in 0.01 N solutions: 1 –CsF, 2 –NaF. 400 Hz. 25$±$0.1°

Figure 2: Fig. 2. Curves of differential capacitance in 0.01 N solutions: 1 –CsF, 2 –NaF. 400 Hz. 25$±$0.1°

sodium and cesium iodides. The data obtained for 0.9 and 0.01 N solutions are presented in Figs. 1 and 2. The capacitance values measured in NaF solutions are in good agreement with the data of D. Grahame (^{6}), with the exception of the extremely positive potentials, where, up to $\varphi = +0.25$ V, in contrast to D. Grahame' s data, we did not observe a sharp rise in the differential-capacitance curve. Such a rise was observed by us only in solutions that had been kept for a long time in glass, where it is apparently connected with contamination of the solution by traces of surface-active anions. As can be seen from Figs. 1 and 2, the capacitance values of the double layer in solutions of cesium fluoride in the indicated potential intervals lie above the corresponding values for sodium fluoride. In 0.1 N solutions, results were obtained analogous to the data for 0.9 N solutions of NaF and CsF. In the case of 0.01 N solutions of sodium and cesium fluorides

differences in the capacitance values persist approximately up to the potential $\varphi = 0.0$. At more positive potentials the capacitance values in these solutions

Fig. 1. Curves of differential capacitance in 0.9 N solutions: 1 –CsF, 2 –NaF, 3 –CsJ, 4 –NaJ. 1000 Hz. $25 \pm 0.1°$

coincide within the limits of experimental error. From these data one may conclude that there is greater adsorption of the cesium cation on the surface of mercury on which the fluoride anion is adsorbed, in comparison with the sodium cation; and since the fluoride ion is not adsorbed on mercury in super-equivalent amounts, i.e., no recharge of the mercury surface occurs in the presence of the fluoride ion, the adsorption of the cesium ion cannot be interpreted otherwise than as specific.

Fig. 2. Curves of differential capacitance in 0.01 N solutions: 1 –CsF, 2 –NaF. 400 Hz. $25 \pm 0.1°$

The conclusion of super-equivalent adsorption of Cs^+ can also be reached by comparing the corresponding capacitance curves for the fluorides and iodides of sodium and cesium. Indeed, as is seen from Fig. 1, at sufficiently negative potentials the iodine anion ceases to influence the capacitance, and the values of the differential capacitance for the corresponding iodides and fluorides converge.

However, the potentials at which the capacitance curves merge are not the same and depend on the nature of the cation. Thus, within the accuracy of our measurements, the action of iodine in the case of $0.9\,N$ solutions of NaF and NaJ is manifested up to the potential $\varphi = -1.5$ V; whereas in the case of $0.9\,N$ solutions of CsF and CsJ, up to the potential $\varphi = -1.7$ V, which can be explained only by super-equivalent adsorption of cesium, in the presence of which the adsorption of iodine occurs at more negative potentials than in the case of the sodium cation. An analogous result was obtained in the case of the corresponding $0.1\,N$ solutions of the fluorides and iodides of sodium and cesium.

The conclusion that super-equivalent adsorption of the cesium cation occurs is also supported by the data on the p.z.c. values measured by us on an amalgamated mercury jet electrode after preliminary purification of the solution by prolonged polarization at a mercury cathode. The values obtained were corrected for diffusion potentials according to Henderson’ s equation, using mobilities at infinite dilution (see Table 1).

Table 1

Solution	NaF 0.9 N	NaF 0.1 N	NaF 0.01 N	CsF 0.9 N	CsF 0.1 N	CsF 0.01 N	NaJ 0.9 N	NaJ 0.1 N	CsJ 0.9 N	CsJ 0.1 N
$-\varphi_{\text{p.z.c.}}$	0.4724	0.4733	0.473	0.4694	0.4723	0.473	0.799	0.726	0.812	0.732
Same, according to D. Grahame	0.4716	0.4736	0.4735							

As is seen from Table 1, in fluoride solutions a small shift of the p.z.c. toward positive potentials is observed on going from Na^+ to Cs^+, which indicates a certain super-equivalent adsorption of the cesium cation*. The shift of the p.z.c. on going from a 0.1 N LiCl solution to a 0.1 N CsCl solution was first found in the work of D. Grahame (7); however, the presence of the specifically adsorbing chloride anion led the author to a different explanation of the observed effect (8). It should be noted that in the case of 0.9 N fluoride solutions the position of the p.z.c. depends on the pH of the medium: the p.z.c. shifts, upon alkalinization of the solution, toward negative potentials. Thus, in the case of NaF, the potential of zero charge is −0.4724 at pH = 7.0, −0.4732 at pH = 7.5, and −0.4740 at pH = 8.5. We were unable to determine the reason for this phenomenon. The data given in the table for 0.9 N NaF and CsF solutions correspond to pH = 7.0.

In the case where the anion is strongly specifically adsorbed, as occurs in iodide

Figure 3 graph: curves of the interfacial tension of mercury in 0.9 N solutions.

Figure 3: Figure 3 graph: curves of the interfacial tension of mercury in 0.9 N solutions.

solutions, adsorption of the cation causes additional adsorption of the anion, which leads, on going from NaJ to CsJ, to a shift of the p.z.c. toward more negative potentials ([9]).

The data we obtained on the super-equivalent adsorption of cesium were confirmed by electrocapillary measurements in 0.9 N solutions of NaF, NaJ, CsF, and CsJ. The results of these measurements are presented in Fig. 3. As is seen from the figure, the curve for CsF lies somewhat below the curve for NaF, and the curve for CsJ appreciably below the curve for NaJ. The difference in the interfacial tension of mercury in NaF and CsF solutions amounts, at the maximum of the electrocapillary curve, to 0.1 dyn/cm and gradually increases as both the positive and the negative potential increase. Thus, at $\varphi = -0.145$ it is 0.3 dyn/cm, and at $\varphi = -1.195$ it is already 2.9 dyn/cm. The lowering of the interfacial tension of mercury here is caused by the greater adsorption of Cs^+ in comparison with Na^+. In the case of iodide salts, the specific adsorption of cesium increases the adsorption of the iodide anion, and the lowering of the interfacial tension of mercury is greater here. It is especially large on the ascending branch of the electrocapillary curve, on which the mercury surface, in the presence of iodide ions, acquires a negative charge that facilitates adsorption of cesium. Thus, at the maximum the difference for NaJ and CsJ solutions reaches 3.4 dyn/cm and increases by $\varphi = -0.55$ V to 8.0 dyn/cm. It is of interest to compare $\Delta\sigma$ at some definite sufficiently negative potential, for example at $\varphi = -1.195$, for the solutions NaF—NaJ and CsF—CsJ. These differences are, respectively, 0.4 and 0.9 dyn/cm, and their distinction indicates a pulling into double layer of iodide anions as a result of the greater adsorption of the cesium cation in comparison with the sodium cation. Finally, an important result of the electrocapillary measurements is the presence of a shift of the maximum on the electrocapillary curve from −0.471 in the case of NaF to −0.468 for CsF and from −0.815 for NaI to −0.833 for CsI. In the case of fluoride solutions these results agree well with the data obtained by us in measurements of the p.z.c. by the method of the streaming electrode. In the case of iodides the p.z.c. values obtained on the streaming electrode lie somewhat more positive than the corresponding

Fig. 3. Curves of the interfacial tension of mercury in 0.9 *N* solutions: 1 —CsF, 2 —NaF, 3 —CsI, 4 —NaI. 22 ± 0.5°.

---

* In 0.01 N NaF and CsF solutions the p.z.c. values measured on the mercury jet electrode agree within the limits of experimental error; however, the minimum on the capacitance curve in 0.01 N solutions shifts by 6 mV toward the positive side on going from NaF to CsF (Fig. 2).

electrocapillary maxima, which is possibly connected with incomplete removal from these solutions of traces of free iodine, which plays the role of a depolarizer; the shift of the p.z.c. on going from NaI to CsI, determined by both methods, proves, however, to be identical.

Received
8 V 1958

CITED LITERATURE

1. A. N. Frumkin, B. B. Damaskin, N. V. Nikolaeva-Fedorovich, DAN, **115**, 751 (1957).
2. D. C. Grahame, B. A. Soderberg, J. Chem. Phys., **22**, 449 (1954).
3. D. C. Grahame, Zs. Electrochem., **59**, 773 (1955).
4. D. C. Grahame, J. Am. Chem. Soc., **68**, 301 (1946).
5. V. I. Melik-Gaikazyan, ZhFKh, **26**, 560 (1952).
6. D. C. Grahame, J. Am. Chem. Soc., **76**, 4819 (1954).
7. D. C. Grahame, J. Electrochem. Soc., **98**, 343 (1951).
8. D. C. Grahame, E. M. Coffin, J. I. Cummings, M. A. Poth, J. Am. Chem. Soc., **74**, 1207 (1952).
9. A. N. Frumkin, V. N. Nikolaeva-Fedorovich, Vestn. MGU, ser. mech., astron., math., phys., chem., No. 4, 169 (1957).

Note: Figure translations are in progress. See original paper for figures.