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Abstract

Full Text

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MEASUREMENTS OF THE DIFFERENTIAL CAPACITANCE OF THE DOUBLE ELECTRIC LAYER ON A DROPPING MERCURY ELECTRODE IN SOLUTIONS OF KF, LiCl, NaCl, AND KCl IN METHYL ALCOHOL

(Presented by Academician A. N. Frumkin, 2 I 1958)

In our investigations we considered it a very important question whether the different polarizing ability of ions* influences the structure of the double electric layer and its capacitance.

Measurements carried out with aqueous solutions of salts of alkali metals showed that the differential capacitances of the double electric layer on a dropping mercury electrode in solutions containing the ions Li^+, Na^+, K^+ differ only slightly and, at a potential of about -1.1 V, are from 15.5 to 16.5 $\mu F/cm^2$. They increase only slightly with increasing applied potential ([1,2]).

Taking into account that the compressibility of methyl alcohol molecules in the dense part of the double electric layer is approximately three times greater than the compressibility of water molecules, we assumed that the interaction of ions with the electrode in methyl alcohol would be stronger than in water and, consequently, that the effect of the different polarizing ability of the ions would be more readily detectable ([3]).

On the basis of the measurements carried out by us (the method of measurement was described by us earlier ([4])) with 0.1 N solutions of LiCl, NaCl, and KF and with a saturated (approximately 0.05 N) KCl solution in methyl alcohol, it may be concluded that, at sufficiently large negative potentials, above -1.2 V, differences in capacitance appear (Fig. 1).

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Fig. 1. Differential capacitances of solutions of KF (a), LiCl (b), NaCl (c), KCl (d) in methanol as a function of potential.

The appended diagram of the dependence of the differential capacitance on potential shows that the capacitance at a given value of the potential is the greater, the smaller the polarizing ability of the cations.

* By the polarizing ability of ions, according to Born and Heisenberg, we mean the ratio of the ionic charge to the square of its radius. Its value is equal to 1.7 for Li^+, 1.0 for Na^+, and 0.6 for K^+.

It follows from the approximate measurements that cations possessing the same polarizing ability should, at the same applied potential, cause the formation of an electrical double layer of the same capacitance.

The fact that the negative branch of the KCl curve lies below the negative branch of KF is connected with the difference in the concentrations of the solutions used. As our measurements showed, the negative branch of the differential-capacitance curve of saturated, i.e. approximately $0.05N$, KCl practically coincides with the negative branch of $0.05N$ KF.

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