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CAPACITY OF THE DOUBLE LAYER OF THE MERCURY ELECTRODE IN DILUTE SOLUTIONS OF HYDROCHLORIC ACID AND OF POTASSIUM CHLORIDE

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The method described in the last paper was used to plot the capacity curves of a mercury electrode in dilute solutions of hydrochloric acid and of potassium chloride. The mercury used was twice distilled. The potassium chloride was from Kahlbaum, the brand «for analysis». It was purified from organic substances by heating it red hot. The water used in preparing the solution was twice distilled and had a conductivity of from 0.7×10^{-6} to 0.9×10^{-6} mho. The hydrochloric acid solutions were prepared from freshly produced hydrogen chloride. The electrolytic cell for measuring the polarization capacity on mercury was made of Jena glass, about 400 cm^3 in volume. The main parts of the cell are as follows: a dish filled with mercury, in which the surface area of the mercury is 36.3 cm^2; there is a platinized platinum gauze over the surface of the mercury which serves as auxiliary electrode; a calomel electrode prepared with the same solution was used for comparison. The potential of the calomel electrode when the concentration of the hydrochloric acid was 10^{-4} n, was unstable, and therefore it was necessary to compare it with a normal calomel electrode and make respective corrections in measuring the capacity curves. The electrolytic cell was joined to the hydrogen apparatus by means of a ground glass joint. Before the experiment electrolytic hydrogen was passed from a spiral tube submerged in liquid air through all the parts of the cell for 3—4 hours. None of the ground glass joints nor taps were greased, but just wetted with the same solution.

Since there is a platinized platinum screen in the cell serving as auxiliary electrode, when it is saturated with hydrogen, hydrolytic adsorption of the salts from the solution is possible, liberating acid, which may affect the conductivity of dilute potassium chloride solutions. Our measurements of the conductivity of a 10^{-3} n potassium chloride solution did not show any noticeable difference before and after the experiment, however when the concentration was 10^{-4} n a difference could be observed.

The distance between the mercury and the auxiliary electrodes could be regulated by varying the level of the mercury. The resistance of the solution which filled up the space between the mercury and the platinum screen was measured while plotting the capacity curve, whereby use was made of a current of higher frequency. We plotted the capacity curves for the following solutions: 1 n KCl, 10^{-1} n KCl, 10^{-2} n KCl, 10^{-3} n KCl, 10^{-3} n HCl, 10^{-4} n HCl. The curves given in this paper are the average of a large number of experiments. As mentioned in the last paper, the ohmic corrections were taken into account in calculating the capacities of solutions of low conductivity. Fig. 1 shows the experimental capacity curves of the mercury electrodes where the capacity values are plotted along the ordinate axis, and the potential values of mercury φ referred to a normal calomel electrode—along the abscissa axis. Measurements with alternating current, of course, immediately give the value of differential capacity $\left(\frac{\partial \varepsilon}{\partial \varphi}\right)$, where ε is the charge per unit surface. On the capacity curve of the normal potassium chloride solution there is a small maximum which has already been described before in a paper by Borissova and Proskurnin. The curve of the decinormal solution consists of two almost horizontal branches which correspond to a double layer formed of anions and cations respectively, and a connective branch with intermediate capacity values. At high positive or negative surface charges the capacity value increases due to the deformation of ions. This curve does not give any indication of a diffuse structure. However, a minimum although an indistinct one as yet, appears already on the curve of the 10^{-2} n solution of potassium chloride, near the zero charge point, and in the 10^{-3} and 10^{-4} n solutions this minimum which was observed at $\varphi = -0.53$, in excellent conformity with the determination of the zero charge point according to electrocapillary data, is very distinctly expressed.

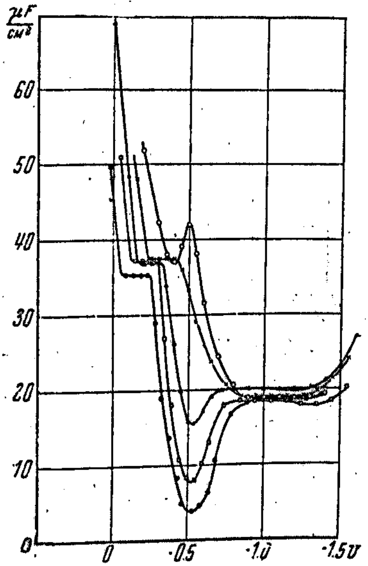

Fig. 1. Capacity of mercury electrode after experimental data: ○○○— norm. KCl; ××× — 0.1 n KCl; ▲▲▲ — 0.01 n KCl; □□□ — 0.001 n KCl; ●●● —0.0001 n KCl.

The minimal capacity value on the curve of the 10^{-2} n potassium chloride solution equals 16 μF, on the curve of 10^{-3} n KCl it equals 7.9 μF, and on the capacity curve of the 10^{-4} n hydrochloric acid solution this value equals 3.9 μF. From Gouy and Stern's theory it follows that the double layer has the most diffuse structure near the zero charge point. When the absolute value of the charge increases, ions are attracted to the surface and the double layer changes in structure from diffuse to non-diffuse. As a result of this the average thickness of the double layer should be a maximum, and the capacity—a minimum at the zero charge point. It was interesting to compare the results of our measurements with the values of $\frac{\partial \varepsilon}{\partial \varphi}$ calculated according to Stern's theory.

Taking for granted that ions are not adsorbed specifically, neglecting the influence of occupying the surface on the adsorption and assuming the thickness of Helmholtz's layer to equal the diameter of a molecule of water, we can write the equation of Stern's theory in the following form:

$$\varepsilon = K(\varphi - \psi_1) = 2cdF \text{ sin hyp } \frac{\psi_1 F}{RT} + 4c\lambda F \text{ sin hyp } \frac{\psi_1 F}{2RT} \qquad (1)$$

where ψ_1 is the potential value at a distance of one ionic radius from the surface of the mercury; d, the diameter of a molecule of water (3.1×10^{-8} cm); λ, the thickness of the ionic atmosphere for a uni-univalent electrolyte at a given concentration according to Gouy-Debye; K, the capacity of the non-diffuse layer; c, the concentration expressed in gram-equiv. per cm^3.

The first and the second term on the right side of equation (1) express, as we know, the charge of the non-diffuse and of the diffuse part of the double layer, respectively. However, equation (1) cannot be used for calculating $\frac{\partial \varepsilon}{\partial \varphi}$ and comparing the value thus obtained with experimental data in the whole interval of measurable potentials, since it assumes that the value K is constant for all values of φ; actually, however, the value of K is doubtless different for a positively and negatively charged surface. Therefore this equation was modified by introducing two capacity values of Helmholtz's layer K_1 and K_2 which are characteristic of a double layer formed of anions and cations, respectively. Under these conditions K of equation (1) should be considered a variable depending upon the concentration of anions and cations in Helmholtz's layer. Since these concentrations are proportional respectively to $\exp \frac{\psi_1 F}{RT}$ and $\exp\left(-\frac{\psi_1 F}{RT}\right)$, the most simple way is to take the value K equal to:

$$K = \frac{K_1 \exp \frac{\psi_1 F}{RT} + K_2 \exp\left(-\frac{\psi_1 F}{RT}\right)}{\exp \frac{\psi_1 F}{RT} + \exp\left(-\frac{\psi_1 F}{RT}\right)}. \quad (2)$$

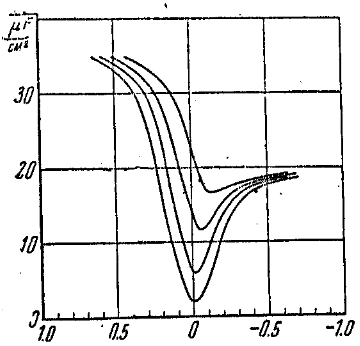

Fig. 2. Capacity of mercury electrode calculated after Stern's theory for a 0.1; 0.01; 0.001 and 0.0001 n solution (from top to bottom).

Equation (2) corresponds to the physical picture of two condensers in parallel, whose capacities per unit area equal K_1 and K_2, and the areas they cover are proportional to the concentrations of anions and cations in Helmholtz's layer. Philpot in the paper mentioned above gave another method of uniting the positive and negative branches, which are expressed by Stern's equation with different values of K, into one whole, lacking a definite physical meaning, however. If we substitute the value of K from (2) in (1), it is not difficult to get the following relations from this equation:

$$\varphi = \psi_1 + \frac{2cdF}{K} \text{ sin hyp } \frac{\psi_1 F}{RT} + \frac{4c\lambda F}{K} \text{ sin hyp } \frac{\psi_1 F}{2RT} \quad (3)$$

$$\frac{\partial \varepsilon}{\partial \varphi} = KA : \left\{A + K - \frac{1}{2}(K_1 - K_2)\frac{(\varphi - \psi_1)F}{RT} \text{ cos hyp}^{-2} \frac{\psi_1 F}{RT}\right\} \quad (4)$$

where

$$A = \frac{2cF^2}{RT}\left(d \text{ cos hyp } \frac{\psi_1 F}{RT} + \lambda \text{ cos hyp } \frac{\psi_1 F}{2RT}\right).$$

From equations (2), (3) and (4) a curve can easily be drawn which gives the capacity value $\frac{\partial \varepsilon}{\partial \varphi}$ as a function of φ. The curves in Fig. 2 were calculated in this manner, taking $K_1 = 38$ μF/cm² and $K_2 = 20$ μF/cm². The values on the abscissa axis in Fig. 2 are counted from the zero charge point. From comparing Figs. 1 and 2 it will be obvious that the general position and form of the curves calculated according to Stern's theory greatly resemble the experimental curves, but the calculated capacity values are situated considerably lower than the observed ones. Thus, for instance, the minimum of observed capacity for the 0.0001 n solution equals 3.9 μF, while calculation according to the equation (4) gives $\frac{\partial \varepsilon}{\partial \varphi} = 2.15$ and according to Gouy's theory of the diffuse layer—2.36 μF. Thus, it may be concluded that the real double layer is less diffuse than should be expected according to theory.

This deviation shows that there are specific attractive forces, i. e. attractive forces which do not depend upon the charge, between the metallic surface and the ions. This adsorption effect, however, cannot be identical to that which is observed at higher concentrations. Indeed, high capacity values are observed to both sides of the zero charge point, i. e. the interaction mentioned should be ascribed to both cations and anions, while it is well known from electrocapillary data that at higher concentrations inorganic cations show negative and not positive adsorption. It must be assumed that we have to do here with attraction which turns into repulsion at short distances. It is possible that at large distances those image forces are manifested which were postulated by Gurney and which for reasons as yet unknown are not observed when the ions are in the immediate vicinity of the surface of the mercury electrode.

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