PROBLEM OF APPLICABILITY OF THE GOUY-CHAPMAN THEORY TO THE DIFFUSION LAYER IN THE CASE OF A GALLIUM ELECTRODE

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In a previous communication [1] we made an attempt to verify the applicability of Grahame's ideas [2] to the independence of the dense layer capacity of the concentration of the nonadsorbed electrolyte for dilute

$$HClO_4 + NaClO_4$$

solutions on gallium. The selection of the given system was conditioned by the fact that the ClO_4^- anion is not adsorbed specifically at the gallium–electrolyte interface. However, the comparison of the evaluated and experimental C-versus-q curves (C is the differential capacity, q is the electrode charge) has revealed a certain discrepancy between them which was explained by suggesting a change of the capacity of the dense layer on gallium, produced by the disintegration of the structure of the adsorbed water layer by ClO_4^- anions.

It was interesting to verify the Gouy-Chapman theory applying the method suggested by Parsons [3]. This author used the equation

$$1/C = 1/C_G + 1/C_D, \tag{1}$$

where C is the capacity measured experimentally; C_G is the capacity of the dense layer and C_D is the capacity of the diffusion layer, evaluated according to the Gouy-Chapman theory. In accordance with [4] C_D was taken to be

$$C_D = 19{,}49\sqrt{137c + q^2} \tag{2}$$

(where c is the concentration of the electrolyte). Parsons has represented the dependence of 1/C on $1/C_D$ graphically. A straight line with a unit gradient must be obtained for any charge of the electrode without dependence on the concentration on the assumption that no specific adsorption exists. The section on the ordinate is $1/C_G$. In the case of a mercury electrode this relationship is actually realized.

In Fig. 1 the functions 1/C versus $1/C_D$ are shown for gallium: 1 is the straight line calculated on condition that C_D is defined by Eq. (2) and C_G is 77.8 $\mu F/cm^2$; and 2 are the experimental capacity values on gallium for the $HClO_4 + NaClO_4$ system. From Fig. 1 it is evident that the experimental values of 1/C keep satisfactorily to a straight line. But the gradient of the straight line differs slightly from the unit. For a coincidence of the given straight lines, the capacity of the diffusion layer for all concentrations on gallium should be much higher than that calculated according to the Gouy-Chapman theory. The only parameter which can be responsible for this is the dielectric constant in the diffusion layer (C_D is proportional to $D^{\frac{1}{2}}$ and D is supposed equal to the volume value).

In the given case the calculated value D was 120, i.e., 1.5 times higher than in the bulk of the solution. Figure 2 demonstrates the C-versus-q curves, calculated according to Grahame's method [2] for the 0.035 N solution. In the first case (curve 1) C_D was calculated using Eq. (2). The capacity of the diffusion layer in the case of curve 2 was calculated according to the value obtained, D = 120. C_G was derived from the experimental values of the capacity in 0.1 N $NaClO_4$. From Fig. 2 it is evident that the dots corresponding to the experimental capacity values for the 0.01 N $HClO_4$ + 0.025 N $NaClO_4$ solution coincide satisfactorily with curve 2, i.e., in the given range of surface charges, D in the diffusion layer keeps its constant value of 120.

For the time being, it is impossible to give a sufficiently definite explanation for the result obtained; however, to a certain extent, it is in keeping with the notion on the spreading of the influence of the hydrophilic solid surface to distances surpassing the monolayer of the water molecules, expressed repeatedly in literature by B. V. Deryagin.

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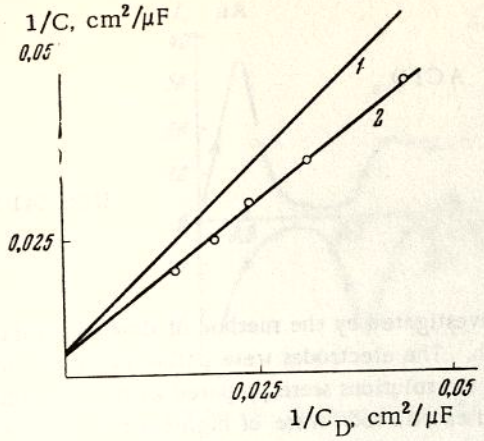

Fig. 1

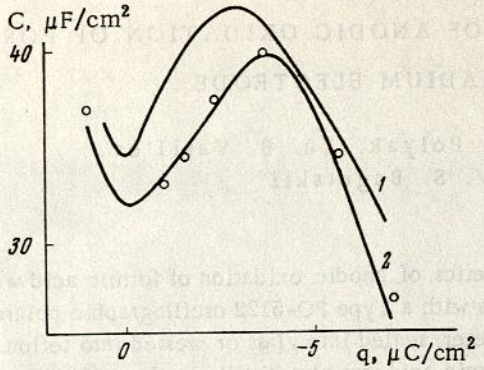

Fig. 2

Fig. 1. Functions $1/C$ versus $1/C_D$: 1) evaluation when $C_G = 77.8$ and C_D is defined by Eq. (2); 2) experimental values (dots) for the $HClO_4 + NaClO_4$ system.

Fig. 2. C-versus-q curves for 0.035 N solution: 1) C_D defined by Eq. (2); 2) C_D calculated with D = 120. The dots represent the experimental capacity values.

It should be mentioned that the range of variation of the concentrations was sufficiently restricted (from 0.01 to 0.1) which corresponded to a change of thickness in the diffusion layer by merely 3.17 times. Unfortunately, owing to experimental difficulties, it was not possible to extend this range toward higher dilutions by which the effect of the influence of the metal on the water molecules in the diffusion layer should have been markedly reduced.

LITERATURE CITED

1. A. N. Frumkin, N. B. Grigor'ev, and I. A. Bagotskaya, Élektrokhimiya, 2, 329 (1966).
2. D. C. Grahame, Chem. Rev., 41, 441 (1947).
3. R. Parsons and F. G. R. Zobel, J. Electroanalyt. Chem., 9, 333 (1965).
4. M. A. V. Devanathan, Trans. Faraday Soc., 50, 373 (1954).