# STRUCTURE OF THE DOUBLE ELECTRIC LAYER ON EUTECTIC ALLOY In – Ga IN WATER AND ACETONITRILE

## II. STRUCTURE OF THE DOUBLE ELECTRIC LAYER IN DILUTE AQUEOUS SOLUTIONS OF ELECTROLYTES AND THE EFFECT OF TEMPERATURE ON THE DIFFERENTIAL CAPACITANCE

N. B. Grigor'ev, S. A. Fateev,
and I. A. Bagotskaya

UDC 541.13

This article gives data on the structure of the double electric layer on eutectic alloy In–Ga in dilute solutions of $H_2SO_4$, $HClO_4$, NaF, and HCl in water at 32°C, obtained by measuring the differential capacitance, and on the effect of temperature (25-85°C) on the differential capacitance on In–Ga alloy in 0.01 N $HClO_4$ and 1 N $Na_2SO_4$ and on gallium in 1 N $Na_2SO_4$. The purity of In and Ga, the procedures used for preparing the alloy, operating the In–Ga and gallium dropping electrodes, and measuring the differential capacitance were the same as in [1]. The reference electrode was a s.c.e. at the experimental temperature.

Figure 1 shows the differential capacitance curves in $HClO_4$ solutions of various concentrations.* It will be seen that with decreasing $HClO_4$ concentration the $C-\varphi$ curves exhibit minima, the depth of which increases with dilution. The dependence of the depth of the minimum on the solution concentration enables us to relate it to the diffuseness of the double electric layer and to determine the zero-charge potential of the electrode $\varphi_0$ from the value of the minimum potential $\varphi_{min}$. In $HClO_4$ solutions, $\varphi_{min} = \varphi_0 = -0.96$ V and is independent of the $HClO_4$ concentration. In 0.01 N and 0.001 N $H_2SO_4$ solutions, $\varphi_{min} = -0.98$ V and likewise is independent of the $H_2SO_4$ concentration. Making a correction for electrolyte asymmetry, in dilute $H_2SO_4$ $\varphi_0$ is located at $-0.95$ V. The data show that in dilute $HClO_4$ and $H_2SO_4$ solutions the zero-charge potentials are close and coincide with the $\varphi_0$ values in 1 N $NaClO_4$ and $Na_2SO_4$ solutions, determined in [1] by inverse integration of the $C-\varphi$ curves and in [2] by the method of electrocapillary curves. According to [1, 2], in 1 N $NaClO_4$ $\varphi_0 = -0.96$ V, and in 1 N $Na_2SO_4$, $-0.96$ V [1] or $-0.94$ V [2]. It therefore follows that $ClO_4^-$ and $SO_4^{2-}$ anions are not adsorbed specifically on In–Ga alloy and that we may take a potential of $-0.95$ to $-0.96$ V (with respect to a s.c.e.) as the zero-charge potential of In–Ga alloy in water (the zero-charge potential of gallium in water is $-0.98$ V [3], and that of indium is $-0.93$ V [4], with respect to a s.c.e.).

In 0.01 N HCl and NaF, $\varphi_{min}$ is located at $-1.00$ and $-1.03$ V, respectively, and is therefore more negative than in dilute solutions of $H_2SO_4$ and $HClO_4$. This indicates specific adsorption of $Cl^-$ and $F^-$ anions; $F^-$ is not adsorbed specifically on an indium electrode [4]. The difficulties resulting from the necessity of acidifying the solutions at potentials close to $\varphi_0$ did not allow us to investigate adsorption of $F^-$ on gallium. Indirect data on specific adsorption of $F^-$ on gallium were obtained by Popova et al. [5], who investigated the effect of halide anions on passivity of gallium.

To verify the applicability of the Gouy-Chapman theory to the diffusion layer in the case of an In–Ga electrode, calculations were made (following Grahame [6]) for the $C-\varphi$ curves measured in $HClO_4$. The dense-layer capacitance $C_g$ was determined from experimental data for a 0.1 N solution. The calculated $C-\varphi$ curves were compared with the experimental curves for 0.01 and 0.001 N $HClO_4$ solutions (Fig. 1). Very satisfactory agreement was obtained at potentials close to $\varphi_0$. This indicates that the Gouy-Chapman

---

*In [1] we showed that on In–Ga alloy at potentials close to the zero charge potential the differential capacitance curves measured in solutions of acids and neutral salts with the same anion coincide and are independent of the ac frequency.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 8, No. 11, pp. 1633-1635, November, 1972. Original article submitted February 15, 1972.

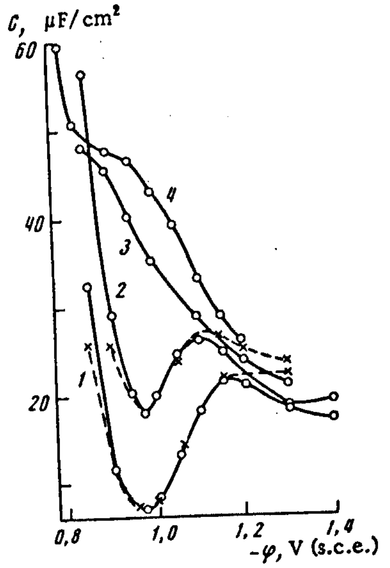

Fig. 1

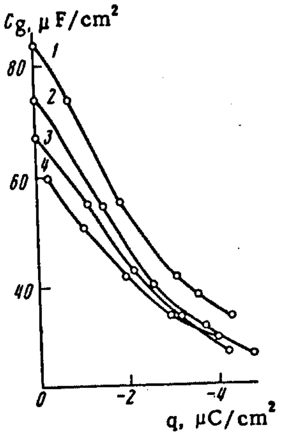

Fig. 2

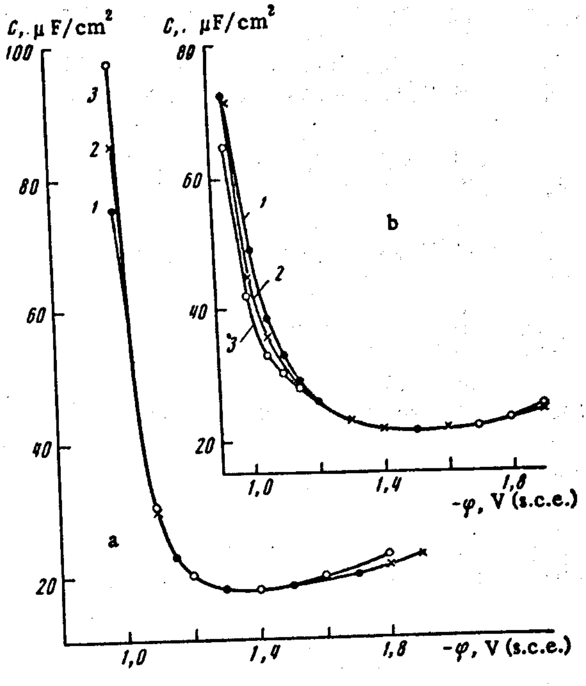

Fig. 3

Fig. 1. Experimental (solid curves) and theoretical (dashed lines) differential-capacitance curves on eutectic alloys In–Ga in $HClO_4$ solutions of different concentrations: 1) 0.001; 2) 0.01; 3) 0.1; 4) 1 N.

Fig. 2. Dense-layer capacitance $C_g$ vs charge on In–Ga eutectic alloy q at: 1) 25; 2) 45; 3) 65; 4) 85°C.

Fig. 3. Differential capacitance curves on In–Ga eutectic alloy (b) and gallium (a) in 1 N $Na_2SO_4$ + 0.01 N $H_2SO_4$ at: 1) 30; 2) 60; 3) 80°C, measured at ac frequency 5000 Hz.

theory is applicable to the diffusion layer for an In–Ga electrode and also confirms the absence of specific adsorption of the $ClO_4^-$ anion.

Our previous communication [1] showed that as far as the double-electric-layer structure and adsorption properties are concerned, an In–Ga electrode is intermediate between mercury and gallium and that as in the case of gallium, at low negative or positive charges, on an In–Ga electrode we observe specific adsorption of water molecules with the negative end of the dipole facing the electrode surface. Rybalka [7] showed that important information on the reaction of a solvent with an electrode may be obtained from data on the temperature dependence of the dense-double-layer capacitance $C_g$. Thus, on a cadmium electrode [8] in a solution of an inactive electrolyte, at small negative surface charges, corresponding to specific adsorption of water, the relative decrease of the dense-layer capacitance with temperature is less than on mercury [9].

Figure 2 shows the $C_g$–q curves for an In–Ga electrode at different temperatures calculated from the C–φ curves in 0.01 N $HClO_4$. It will be seen that with increasing temperature the dense-layer capacitance on In–Ga alloys decreases, as in the case of cadmium and mercury. On an In–Ga electrode the relative changes in the capacitance with temperature at q = const are less than on mercury but greater than on cadmium. A comparison of the $C_g$–q curves on In–Ga alloy and gallium at different temperatures is impossible because of the inapplicability of the Gouy-Chapman theory to a gallium electrode in aqueous solutions [10]. Figure 3 shows the C–φ curves on gallium and In–Ga alloy at different temperatures measured in an acidified 1 N $Na_2SO_4$ solution, in which the double-electric-layer capacitance approaches that of the dense part of the layer. It will be seen that on an In–Ga electrode the effect of temperature on the differential-capacitance curve is greater than on gallium. At the present moment we are not in a position to give an unambiguous interpretation of our data on the temperature dependence of the capacitance. This would require more experimental data.

We would like to take this opportunity to thank Academician A. N. Frumkin for discussing the results.

## LITERATURE CITED

1. N. B. Grigor'ev, S. A. Fateev, and I. A. Bagotskaya, Élektrokhimiya, 8, 1525 (1972).
2. N. S. Polyanovskaya and A. N. Frumkin, Élektrokhimiya, 6, 246 (1970).
3. A. N. Frumkin, N. B. Grigor'ev, and I. A. Bagotskaya, Élektrokhimiya, 2, 329 (1966); A. M. Morozov, N. B. Grigor'ev, and I. A. Bagotskaya, Élektrokhimiya, 2, 1235 (1966).
4. N. B. Grigor'ev, I. A. Gedvillo, and N. G. Bardina, Élektrokhimiya, 8, 409 (1972).
5. T. I. Popova, N. A. Simonova, and L. M. Dubova, Élektrokhimiya, 8, 246 (1972).
6. D. C. Grahame, Chem. Rev., 41, 441 (1947).
7. K. V. Rybalka, Élektrokhimiya, 7, 242 (1971).
8. V. A. Panin, K. V. Rybalka, and D. I. Leikis, Élektrokhimiya, 8, 1507 (1972).
9. D. Grahame, Proc. Fourth Electrochemical Conference [Russian translation], Izd. AN SSSR, Moscow (1959), p. 27.
10. A. N. Frumkin and N. B. Grigor'ev, Élektrokhimiya, 4, 533 (1968).