DETERMINATION OF THE NULL-CHARGE POINT OF GALLIUM THROUGH DIFFERENTIAL CAPACITY MEASUREMENTS IN DILUTE SOLUTION

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Measurement has been made of the differential capacity of the dropping gallium (purity, 99.9998%) electrode in dilute HCl + KCl, HCl + KBr, HCl + KI, $HClO_4$, and $NaClO_4$ solutions, working at frequencies ranging from 300 cps to 30 kc/sec.

The differential capacity curves for gallium each pass through a minimum, the depth of the latter being determined by the concentration of the electrolyte. The minimum in halide ion solutions is at higher concentrations than for mercury, this being the result of a lower ion adsorption and higher compact layer capacity in the case of gallium.

The minimum falls at the same point in dilute halide ion and ClO_4- ion solutions, and marks out the null-charge potential for gallium in water. The value obtained for the null-charge potential agrees with that determined from electrocapillary curves.

Calculation was made of the compact layer capacity in $HClO_4$ solutions of various concentrations. It was found that the capacity of the compact layer changes markedly with an alteration in the ClO_4- ion concentration when the surface charge of the gallium is low.

The theory of the double electric layer suggests that the null-charge potential (ncp) can be determined from the position of the minimum on a differential capacity curve developed in a dilute solution of an electrolyte which is either not adsorbed at all, or is adsorbed only weakly [1-4]. Comparison of the predictions of the double layer theory with experimental data has been made only for mercury and thallium amalgam electrodes [5, 6].

The null-charge potential of gallium in 1 N solutions has already been determined from the electrocapillary curves [7, 8]. We ourselves have determined the ncp of this element [9] through the Grahame method [10] of integrating the capacity curve, the values obtained by these two thermodynamic procedures being consistent, the one with the other. It was of interest to compare these results with ncp's obtained from the position of the capacity minimum in dilute solution, which is to say, with results following from a nonthermodynamic method. It is clear that such comparison must be made for solutions of the same composition and concentration.

Differential capacity curves for the dropping gallium electrode were developed in dilute solutions of x HCl + y KCl, x HCl + y KBr, x HCl + y KI, and x $HClO_4$ + y $NaClO_4$. Measurements with dilute halide ion solutions had added interest in so far as these ions are less strongly adsorbed on gallium than on mercury [8, 9], so that the minimum could be expected to fall at a higher concentration on the gallium differential capacity curve than on the corresponding curve for mercury. Measurements in ClO_4- ion solutions were of interest in view of the fact that electrocapillary measurements had shown these ions to be negatively adsorbed on gallium and positively adsorbed on mercury.

The method of measuring the differential capacity was essentially that described in [9]. It has been shown in [11] that a symmetrical arrangement of the working and auxiliary electrodes is a matter of importance in dealing with dilute solutions where the ohmic resistance is high. Special attention was given to this point. The end of the capillary was ground to conical tip of 1 mm external diameter, in order to avoid screening of the drop by the capillary. The fact that the capacity was independent of the frequency of the alternating current in 0.008 N $HClO_4$

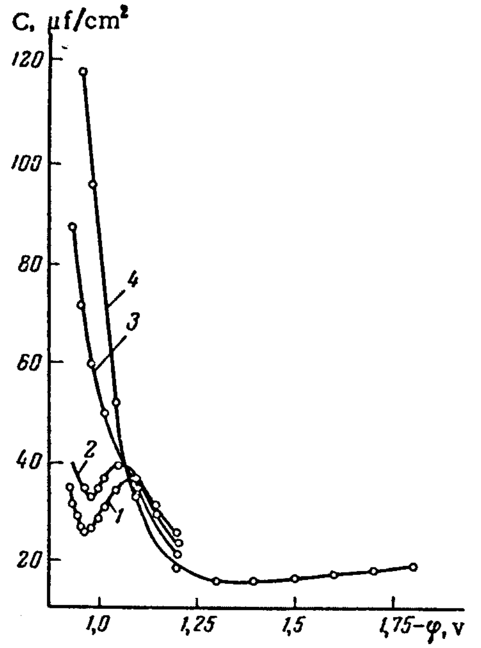

Fig. 1

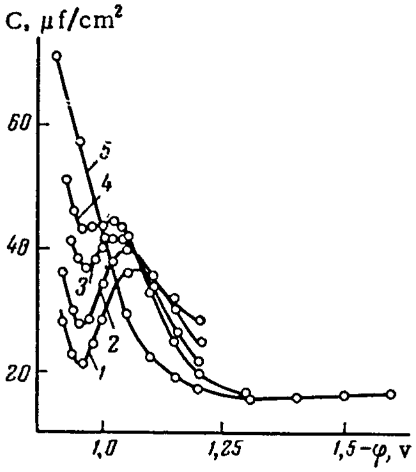

Fig. 2

Fig. 1. Differential capacity in xHCl + yKCl solutions plotted against the electrode potential: 1) x = 0.006 N, y = 0; 2) x = 0.01 N, y = 0; 3) x = 0.008 N, y = 0.042 N; 4) x = 0.008 N, y = 0.092 N.

Fig. 2. Differential capacity in $xHClO_4 + yNaClO_4$ solutions plotted against the electrode potential: 1) x = 0.01 N, y = 0; 2) x = 0.008 N, y = 0.012 N; 3) 0.008 N, y = 0.042 N; 4) x = 0.008 N, y = 0.092 N; 5) x = 0.01 N, y = 1 N.

solution was indication that dispersion of the capacitance values from this source had been eliminated. The maximum resistance in these measurements was less than 400 Ω. The reagents were prepared by the methods outlined earlier in [9]. The gallium had a purity of 99.9998%. The experiments were carried out at 32°C. A normal calomel electrode was used as reference. The measurements in the neighborhood of the minimum were made with the solution acidified to prevent the formation of an oxide film on the gallium surface and at the same time retard anodic dissolution of the metal.

The minimum capacity rose and became dependent on the frequency of the current when the acid concentration dropped below 0.006 N. The minimum was, at the same time, displaced toward the side of negative values. Differential capacity curves for gallium in xHCl + yKCl solutions of various concentrations are shown in Fig. 1, and the corresponding curves for $xHClO_4 + yNaClO_4$ solutions in Fig. 2. Figure 3 presents a comparison of differential capacity curves in solutions containing Cl^-, Br^-, and I^- ions at 10^{-3} N concentration.

It is seen from Fig. 1 that the minimum on the differential capacity curves in xHCl + yKCl solutions is most clearly expressed with 0.006 N HCl ($C_{min} \approx 26 \mu f/cm^2$), gradually diminishes as the acid concentration is increased, and completely disappears at 0.1 N concentration. The fact that the depth of the minimum is dependent on the concentration is indication of its relation to the diffuse double layer in the neighborhood of the null-charge point. The fact that the potential at the minimum is displaced in the negative direction as the concentration is increased gives indication of a Cl^- ion adsorption in these solutions.

It has been pointed out above that the halide ions are less strongly adsorbed on gallium than on mercury. The capacity measurements in dilute Cl^-, Br^-, and I^- ion solutions confirm this conclusion. It has been shown in [12] that specific adsorption makes the double layer less diffuse and, at the same time, increases the minimum capacity. The result is that a minimum can be observed for mercury in contact with Br^- and I^- ions only if the concentrations of the ions are quite low, 10^{-3} N in the case of KBr and 10^{-5} N in the case of KI; according to [12], the minimum disappears completely when the concentrations of these solutions become 10^{-2} N and 10^{-4} N, respectively. Because of a lower adsorption of the halide ions, the capacity of the diffuse part of the double electric layer on gallium increases more gradually than was the case with mercury, and the minimum therefore appears at higher concentrations.

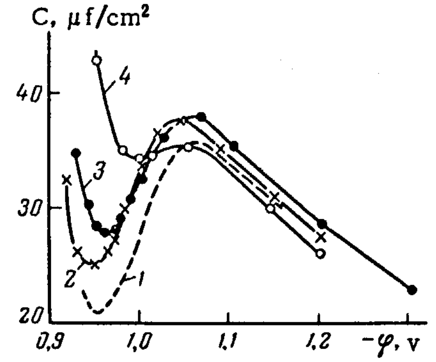

Fig. 3. Differential capacity vs potential curves for solutions of: 1) 0.008 N $HClO_4$; 2) 0.008 N $HClO_4$ + 0.001 N KCl; 3) 0.008 N $HClO_4$ + 0.001 N KBr; 4) 0.008 N $HClO_4$ + 0.001 N KI.

Values of the Minimum Capacity in xHCl + yKCl and x$HClO_4$ + y$NaClO_4$ Solutions of Various Concentrations

C, μf/cm²	0,006 N	0,01 N	0,05 N	0,1 N
Cl^-	26,0	33,0	—	—
ClO_4^-	19,0	20,9	37	43,4

This effect is favored by the fact that the capacity of the compact part of the double electric layer is higher for gallium than for mercury. In actuality, Fig. 3 shows that a minimum could be observed in a 10^{-3} N KI solution. Passage from I^- to Cl^- at fixed concentration reduces the minimum capacity by diminishing the anion adsorption, and the minimum itself is displaced toward negative potential values.

The differential capacity curve for a 0.09 N + 0.01 N $HClO_4$ (Fig. 2) shows a weakly expressed minimum in the neighborhood of the ncp, wheras an analogous curve for mercury in a solution of the specifically inactive F^- ion of the same concentration shows no minimum at all. A minimum in the neighborhood of the ncp is also observed with a 40% thallium amalgam in 0.1 N NaF solution, the capacity of the compact part of the double layer being higher than in the case of mercury.

The capacity at the minimum in x $HClO_4$ + y $NaClO_4$ solutions is less than in x HCl + y KCl solutions of the same concentration, and the potential corresponding to the minimum somewhat displaced toward positive values (Figs. 1 and 2, the table). The potential of the minimum in highly dilute solution is at −0.97 v, which is close to the value obtained in dilute Cl^- ion solutions (−0.98 v) and can therefore be taken as the null-charge point in water where there is no distortion for specifically adsorbed ions.

It should be noted that the value obtained for the potential of the minimum on the differential capacity curves in dilute Cl^- and ClO_4^- ion solutions is close to the ncp value, $\varphi_0 \approx 0.98$ v, obtained from electrocapillary curves by A. M. Morozov in the Institute of Electrochemistry of the Academy of Sciences, USSR.

Grahame has shown [11] that the capacity of the compact layer C_C, varies with the electrode surface charge ε, and is independent of the electrolyte concentration, c, when the system is free of specifically adsorbed ions. The differential capacity can be represented as a pair of series connected condensers, the one equivalent to the compact portion of the double layer and the other equivalent to the diffuse portion of this layer.

$$1/C = (1/C_\Gamma) + (1/C_D), \tag{1}$$

C being the total measured capacity, and C_D the capacity of the diffuse layer as calculated from the equation (see [13])

$$C_D = 19.49\sqrt{137.8\ c + \varepsilon^2}. \tag{2}$$

We have attempted to show the applicability of the Grahame theory of the independence of C_C and solution concentration to the gallium electrode in x $HClO_4$ + y $NaClO_4$ solutions, by calculating C_C for various ClO_4^- ion concentrations. The measurements of A. M. Morozov have shown that ClO_4^- ions increase the boundary potential voltage at the ncp in concentrated solutions, and are thus not specifically adsorbed. The calculations were carried out by transferring the experimentally developed differential capacity curves over to functions with the surface charge as the independent variable, the charge corresponding to fixed potential being obtained by graphic integration of the equation:

$$\varepsilon = \int_0^{\varphi} C\, d\varphi. \tag{3}$$

The compact layer capacity, C_C, was then obtained from Eq. (1) by drawing on the experimentally determined differential capacity and the calculated values of C_D corresponding to the various concentrations. The results of this part of the work are shown in Fig. 4. It is seen that the C_C value for gallium changes radically with the ClO_4^- ion concentration at low charge.

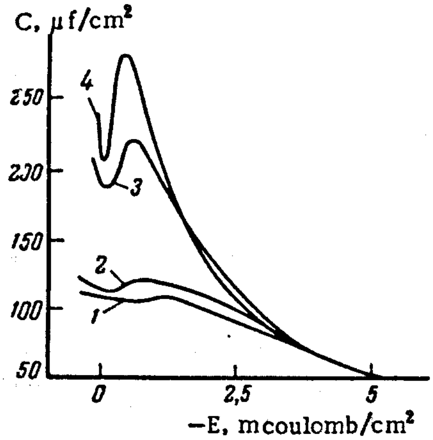

Fig. 4. The relation between the capacity of the compact layer, C_C, and the surface charge, ε, in solutions of:1) 0.09 N $NaCl_4$ + 0.01 N $HClO_4$, 2) 0.01 N $HClO_4$ + 0.025 N $NaClO_4$, 3) 0.02 N $HClO_4$, 4) 0.01 N $HClO_4$.

The variation of the capacity of the compact layer on gallium in ClO_4- ion solutions is, however, radically different from that observed for mercury when it is a matter of specific anion adsorption. Here the pair of series connected condensers (Eq. (1)) is no longer an equivalent circuit and must be replaced by the circuit proposed by Devanathan [13]. Formal calculations based on Eq. (1) lead either to an increase of the compact layer capacity with an increase in the anion concentration, or to negative values of C_C. For the case of gallium, C_C diminishes as the ClO_4- ion concentration is increased. Such an effect could be explained by postulating a breakdown in the structure of the adsorbed layer of water molecules under the action of the ClO_4- anions [9].

The theoretically developed C_C vs < ε curve passes through a minimum at the null-charge potential. This indicates that the double layer correction involved in our calculations was not complete, and at the same time, casts doubt on the applicability of Eq. (2) to the diffuse layer on gallium. The situation here possibly traces back to the fact that the breakdown of the water structure extends to greater distances from the metal surface than was the case with mercury. It is also possible that the equivalent circuit which lies at the basis of Eq. (1) must be modified in the case of gallium. The problem will be studied further.

LITERATURE CITED

1. D. I. Leikis and B. N. Kabanov, Tr. inst. fiz. khimii, AN SSSR, vyp., 6, 5 (1957).
2. T. I. Borisova, B. V. Érshler, and A. N. Frumkin, Zh. fiz. khimii, 22, 925 (1948); 24, 337 (1950).
3. V. L. Kheifets, B. S. Krasikov, and V. V. Sysoeva, Dokl. AN SSSR, 109, 586 (1956); Zh. fiz. khimii, 31, 1992 (1957); Dokl. AN SSSR, 114, 826 (1954).
4. B. N. Kabanov, I. L. Kiseleva, and D. I. Leikis, Dokl. AN SSSR, 99, 805 (1954).
5. D. C. Grahame, Chem. Rev., 41, 441 (1947).
6. L. I. Boguslavskii and B. B. Damaskin, Zh. fiz. khimii, 34, 2099 (1960).
7. Sh. Z. Murtazaev and A. V. Gorodetskaya, URSS, 4, 75 (1936).
8. A. N. Frumkin, N. S. Polyanovskaya, and N. B. Grigor'ev, Dokl. AN SSSR, 157, 145 (1964).
9. A. N. Frumkin, N. B. Grigor'ev, and I. A. Bagotskaya, Dokl. AN SSSR, 157, 1957 (1964).
10. D. C. Grahame, E. M. Coffin, I. J. Cummings, and M. A. Poth, J. Chem. Phys., 74, 1207 (1952).
11. D. C. Grahame, J. Amer. Chem. Soc., 68, 301 (1946).
12. M. A. Vorsina and A. N. Frumkin, Zh. fiz. khimii, 17 295 (1943).
13. M. A. Devanathan, Trans. Faraday Soc., 50, 373 (1954).