DIFFERENTIAL CAPACITY CURVES FOR A MERCURY ELECTRODE AT HIGH CONCENTRATIONS OF THE ELECTROLYTE

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We measured differential capacity curves on a mercury electrode in 1-9.3 N solutions of $NaClO_4$, $Ca(ClO_4)_2$, and $CaCl_2$ at temperatures of 25 and 70 deg C. The 9.3 N solutions with negative surface charges show a high increase in capacity, which is explained by partial dehydration of the cations. In strongly concentrated solutions of $Ca(ClO_4)_2$ we observed a drop in capacity at positive charges and a further increase in differential capacity through adsorption-desorption of the ClO_4^- anions at negative surface charges. The temperature dependence of the capacity in strongly concentrated solutions is basically similar to the case of more dilute solutions.

At the present time, a great amount of data are in literature on the capacity of a binary electric layer in electrolyte solutions [1], but the data are limited to measurements in solutions with concentrations not exceeding 3-4 N. The first capacity curve for a very concentrated solution (10 N $CaCl_2$) was apparently given in [2]. In [3] measurements were made of the cathode branches of C, φ-curves (C = differential capacity and φ = potential) on a mercury electrode in 14 N LiCl, which were compared with the corresponding branches of a C, φ-curve for 1 N lithium chloride. The observed increase in capacity when going from 1 N to 14 N LiCl was explained in [3] by partial dehydration of the lithium cations in concentrated electrolyte solutions. It was of interest to study in more detail the regularities governing differential capacity curves in very concentrated electrolyte solutions. As the object of our research, we selected the salts $NaClO_4$, $Ca(ClO_4)_2$, and $CaCl_2$ which possess high solubility in water.

Method of Measurement. Measurements of the differential capacity were made with the help of an ordinary impedance bridge on a mercury drop electrode. The alternating current frequency was 400 and 1000 cps. The absence of variance of the capacity with frequency showed that the capacity measurements were not distorted through leaking of the solution into the capillary tube [4]. As a further check to ensure the absence of this effect, which was most marked at low resistances of the electrolyte [4], a number of measurements were carried out on an electrode in the form of a stationary drop of mercury on the end of an amalgam wire [5]. The electrode potential was measured against a normal calomel electrode joined to the cell via a bridge with a saturated KCl solution. Since there might have been high diffusion discontinuities in the potential during these measurements in the case of the concentrated solutions, the capacity data were not present in the form of C, φ-curves, but C, ε-curves, where ε is the electrode charge. The quantity ε was calculated by numerical integration of the C, φ-curves with the null charge potentials $\varphi_{\varepsilon=0}$ being determined from curves showing $\varphi_{\varepsilon=0}$ v, log c, where c is the salt concentration. Some of the points on these curves were taken from published data, while others were determined by us from the maximum on a plot of the drip period of the mercury electrode against the potential.

The salts $NaClO_4$ and $CaCl_2$ were purified by double recrystallization from doubly distilled water. The salt $Ca(ClO_4)_2$ was made from "chromatographically pure" $CaCO_3$ and $HClO_4$ distilled in vacuum. Before the measurements were made, a purified hydrogen stream was passed through all the solutions. The degree of purity was checked from coincidence of the zero charging current potential with the potential for the maximum drip period of the mercury electrodes.

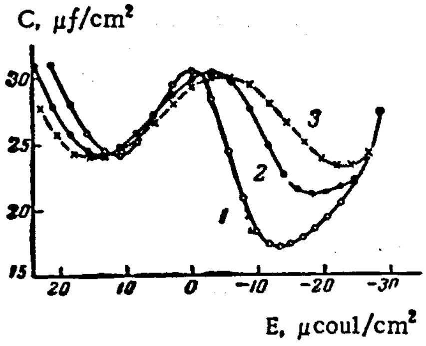

Fig. 1. Differential capacity as a function of electrode charge in solutions $NaClO_4$: 1) 1; 2) 7.1; 3) 9.3 N.

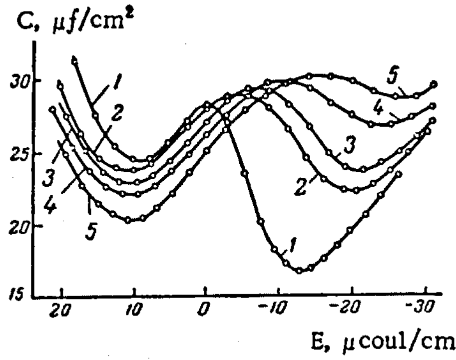

Fig. 2. Differential capacity as a function of electrode charge in solutions $Ca(ClO_4)_2$: 1) 1; 2) 5.8; 3) 6.6; 4) 8.1; 5) 9.3 N.

Results of Measurements and Discussion. As can be seen from Fig. 1, the capacity of a binary layer at $\varepsilon < 0$ increases appreciably as the $NaClO_4$ concentration increases. This result, just as in [3], can be explained by a reduction in the hydrate shell of cations Na^+ in strongly concentrated solutions. At higher negative surface charges, the C, ε-curves for different $NaClO_4$ concentrations coincide. This suggests that under these conditions no water molecules are left between the Na^+-ions and the mercury surface. In this way, the rise in capacity of the cathode branches of the C, φ- or C, ε-curves may be associated with the approach of the Helmholz plane to the electrode surface. On the other hand, the capacity on the anode branch of the C, ε-curve in $NaClO_4$ solutions for not very positive ε does not depend, for practical purposes, on the salt concentration. This may be explained by the fact that the ClO_4^- anions are very slightly hydrated and variation in their concentration in the solution hardly has any effect, therefore, on the thickness of the binary layer via change in the hydrate shell, as observed in the case of cation adsorption at $\varepsilon < 0$.

An interesting regularity is the shift in maximum capacity (hump) in strongly concentrated $NaClO_4$ solutions in the direction of negative charges. As shown in Fig. 1, in 1 N $NaClO_4$ the hump lies at $\varepsilon = 0$, while in 9.3 N solution at $\varepsilon = -5\mu$ coul/cm². In solutions where the anions are very slightly hydrated, and their adsorption on the mercury is governed by the "squeezing" effect [6] (in particular, in perchlorate solutions), the hump on the C, φ- or C, ε-curves is evidently associated with saturation of the polarizability of the water molecule layer lying between the outer Helmholtz plane and the metal surface [7]. According to [7], the capacity component associated with polarizability of the water-molecule layer (C_{H_2O}) may be expressed by the equation:

$$C_{H_2O} = \frac{N\mu^2}{3d^2kT}\,\mathrm{sech}^2\left[\frac{\mu(\varphi - V)}{\sqrt{3}\,dkT}\right], \qquad (1)$$

where N is the number of H_2O molecules per 1 cm² of electrode surface; μ is the dipolar moment of the water molecule, d is the distance from the outer Helmholz plane, φ is the potential counted from the null-charge point, and V is the potential shift due to oriented adsorption of the water molecules. If the hump is at $\varepsilon = 0$, i.e., if $\varphi = 0$, as occurs in a 1 N solution of $NaClO_4$ (Fig. 1), it follows from Eq. (1) that $V = 0$. A shift of the hump toward the negative ε can be explained formally by a change in orientation of the adsorbed water molecules such that V becomes negative. Thus, to explain the position of the hump at $\varepsilon = -5\mu$ coul/cm², we ought to assume that $V = -0.17$ v.

Figure 2 shows data obtained by us in concentrated solutions of $Ca(ClO_4)_2$. Comparison of Figs. 1 and 2 shows that the C, ε-curves in $Ca(ClO_4)_2$ solutions differ appreciably from the corresponding curves in $NaClO_4$ solutions. First, the difference in capacity of the negative branch for different concentrations of $Ca(ClO_4)_2$ is noticeably greater than for $NaClO_4$, so that at $\varepsilon = -30\,\mu$coul/cm², the C, ε-curves for different concentrations do not yet coincide, although the tendency to become closer exists. This result can partially be explained by the high hydration of the two-charge cation Ca^{2+} as compared with the cation Na^+.

Secondly, the capacity on the anode branch of the C, ε-curve, as opposed to the $NaClO_4$ solutions, drops appreciably as the concentration of $Ca(ClO_4)_2$ increases. This result may be associated with the pecularities of the adsorp-

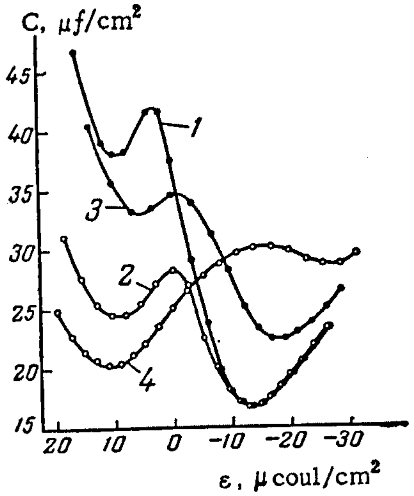

Fig. 3. Differential capacity as a function of electrode charge in solutions: 1) 1 N $CaCl_2$; 2) 1 N $Ca(ClO_4)_2$; 3) 9.3 N $CaCl_2$; 4) 9.3 N $Ca(ClO_4)_2$.

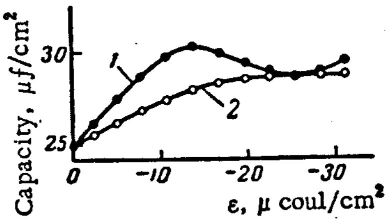

Fig. 4. Differential (1) and integral (2) capacity as a function of electrode charge in a 9.3 N solution of $Ca(ClO_4)_2$.

tion of ions of type ClO_4^-, which are slighly hydrated, disturb the structure of the water and are therefore squeezed onto the surface of the solution in similar fashion to the molecules of organic matter [6]. Indeed, the "squeezing effect" increases with the activity of the electrolyte, and it is just in this respect that $NaClO_4$ and $Ca(ClO_4)_2$ solutions differ from each other very greatly. For example, according to data in [8], the activity factors f in $NaClO_4$ solutions pass through a minimum at which $f = 0.609$ and $m = 2.25$ (m is the molarity), and then slowly increase to 0.677 at $m = 6$. At the same time, f in concentrated $Ca(ClO_4)_2$ solutions ($m = 6$) attain 63.7. In this way, in $Ca(ClO_4)_2$ solutions, we would expect far greater adsorption of the ClO_4^- ions leading to a decline in capacity than $NaClO_4$ solutions. This conclusion is experimentally confirmed. Further confirmation that it is correct can be found from data obtained in [9] for concentrated solutions of $HClO_4$. As is known [8], in concentrated $HClO_4$ solutions there is also a sharp increase in f, while in the anode region of the C, φ-curves we observe a marked reduction in capacity as the $HClO_4$ concentration increases [9].

Finally, as can be seen from Fig. 2, the shifting of the hump toward the negative surface charges is much more clearly marked in $Ca(ClO_4)_2$ solutions than in $NaClO_4$ solutions. For example, in a 9.3 N solutions of $Ca(ClO_4)_2$, the hump comes at $\varepsilon \approx -15$ μcoul/cm². This effect cannot be connected with different degrees of hydration of the Na^+ and Ca^{2+} cations since, as can be seen from Fig. 3, when moving from 1 N to 9.3 N $CaCl_2$ the shift of the hump toward the negative side, just as in $NaClO_4$ solutions, corresponds approximately to a change in ε of 5 μcoul/cm².

It can also be seen from Fig. 3 that anomalies in the strongly concentrated solutions of $Ca(ClO_4)_2$ not only show up in the form of a sudden shift by the hump toward the negative charges, but also in the fact that as distinct from 1 N solutions, the C, ε-curves in the 9.3 N solutions of $Ca(ClO_4)_2$ and $CaCl_2$ do not coincide at negative surface charges, although there is an explicit tendency for them to approach at more negative ε than -30 μcoul/cm². These differences in capacity at $\varepsilon < 0$ cannot be explained by different degrees of hydration of the Ca^{2+} cations in chloride and perchlorate solutions. Indeed, since hydration of the ClO_4^- ions is less than for Cl^- ions, while the activity factors in $Ca(ClO_4)_2$ solutions are greater than in $CaCl_2$ solutions [8], we should only expect an increase in hydration of the Ca^{2+} cations and, consequently, a reduction in the capacity of the binary layer when going from $CaCl_2$ to $Ca(ClO_4)_2$, which, however, does not accord with the experimental data. Apparently, the increased capacity when going from 9.3 N $CaCl_2$ to 9.3 N $Ca(ClO_4)_2$ as well as the sudden shift in the maximum on the C, ε-curves for this solution toward negative ε have the same common cause, which is the imposition on the capacity of a double-layer condenser of an additional capacity due to the adsorption process of the ClO_4^- ions.

Indeed, adsorption of ClO_4^- anions from concentrated $Ca(ClO_4)_2$ solutions, as we have already pointed out, is in many respects analogous to the adsorption of organic molecules. In particular, during adsorption of ClO_4^- ions there is reduction in the capacity of the binary layer. Thus, when the degree to which the surface is filled with ClO_4^- ions varies on the differential capacity curves, we should expect to find desorption maximums. Since there

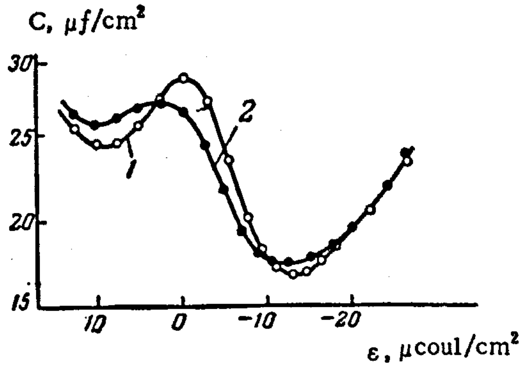

Fig. 5. Differential capacity as a function of electrode charge in 1 N solution $Ca(ClO_4)_2$: 1) at 25 deg C; 2) at 70 deg C.

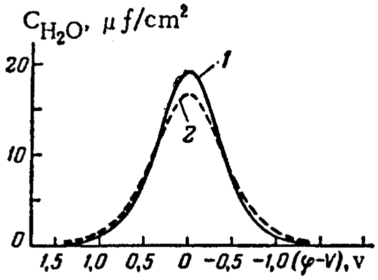

Fig. 6. Capacity associated with polarization of water monolayer as a function of potential calculated from Eq. (1) at $N = 10^{15}$ mol/cm²; $\mu = 1.84$ Debye; d = 4 Å for temperatures: 1) 25 deg C; 2) 70 deg C.

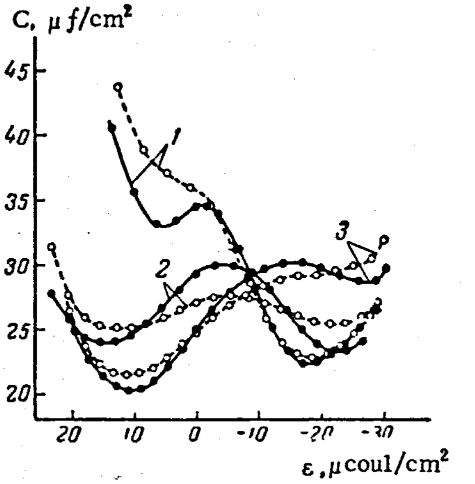

Fig. 7. Differential capacity as a function of electrode charge in 9.3 N solutions: 1) $CaCl_2$; 2) $NaClO_4$; 3) $Ca(ClO_4)_2$ at 25 (solid lines) and 70 deg C (broken lines).

is evidently considerable repulsion between the adsorbed anions, in accordance with [10], the maximums on the differential capacity curves should be very gently sloping. It is only after passage through a gently sloping maximum of this kind that we can expect the C, φ- or C, ε-curves measured in concentrated $Ca(ClO_4)_2$ solutions or any other calcium salt, for example, $CaCl_2$, to come close together. It is indeed these regularities which are observed experimentally (Fig. 3). Further proof of the fact that the maximum on the differential capacity curve in a 9.3 N solution of $Ca(ClO_4)_2$ is not a normal "hump" but an adsorption-desorption maximum is the absence of a maximum on the integral capacity curve in this solution (Fig. 4).

In $Ca(ClO_4)_2$ solutions with concentrations between 1 and 9.3 N we observe a gradual transition from the normal hump, shifted toward the negative ε, to maximum adsorption-desorption. A similar "regeneration of the hump" on C, φ-curves was observed by Kuznetsov and Damaskin in the case of adsorption of $C_3F_7COO^-$ and $C_6F_5COO^-$ anions on a mercury electrode.

Figure 5 shows C, ε-curves for a 1 N solution of $Ca(ClO_4)_2$ at 25 and 70 deg C. Curves of an analogous shape are obtained in an 1 N solution of $NaClO_4$ for the same temperatures. In this way, as distinct from halides [11, 12], the hump is retained in perchlorate solutions at elevated temperatures as well, although it becomes less marked. This result accords with Grahame's data [11], according to which a hump is observed in the capacity curves in the presence of a "similar" NO_3^- anion even at 89 deg C.

It can be easily seen from Fig. 5 that C, ε-curves for perchlorates, measured at different temperatures, intersect twice. This effect, which is much more poorly marked in the case of halides [11, 12] for as yet unclear reasons, tallies well with the Watts-Tobin theory [7]. Indeed, as can be seen from Fig. 6, curves plotting C_{H_2O} against the electrode potential, calculated from Eq. (1) at 25 and 70 deg C, intersect twice. As shown by comparison of Figs. 5 and 7, this effect in strongly concentrated solutions is considerably more marked than in 1 N solutions. In every other respect, the temperature dependence for capacity in strongly concentrated solutions remains essentially the same as in more diluted ones.

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