ELECTROCAPILLARY MEASUREMENTS IN CONCENTRATED $NaClO_4$ SOLUTIONS

B. B. Damaskin, A. N. Frumkin,
V. F. Ivanov, N. I. Melekhova, and V. F. Khonina

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Electrocapillary curves of a mercury electrode in 0.1 to 9.2 N $NaClO_4$ were measured. From the data obtained, the Gibbs surface excesses (Γ) of both the cations, Na^+, and the anions, ClO_4^-, were calculated as functions of electrode charge at various $NaClO_4$ concentrations. The dependence of Γ_- on $NaClO_4$ concentration shows that between the mercury surface and the ions adsorbed on it there exists an interlayer of water molecules at negative as well as at positive charges of the mercury electrode.

In [1], the system mercury/concentrated $NaClO_4$ solution was studied by measuring the differential capacity. Literature data on the activity coefficients in concentrated $NaClO_4$ solutions [2] made it feasible to employ electrocapillary curves as well for an investigation of this system. The results obtained by this method constitute the content of the present communication.

The interfacial tension, σ, was measured by us at room temperature with the aid of a Gouy capillary electrometer, a saturated calomel electrode (sce) serving as reference electrode. The results obtained for 0.1, 1.0, 3.3, 5.5, 7.65, and 9.2 N $NaClO_4$ solutions are given in Table 1. In the same solutions we measured further the potentials of a dropping 0.95 M sodium amalgam electrode (φ_{am}) against sce, and these are given in the last row of Table 1.* It was thus possible to construct electrocapillary curves in (σ, φ^+) coordinates, where φ^+ is the potential relative to a reference electrode reversible to the cation (in the present case, relative to an amalgam electrode in the same solution).

Thereafter the Gibbs surface excess for perchlorate ions (Γ_-) was calculated by graphical differentiation according to the formula [3]

$$\Gamma_- = \frac{1}{2RT}\left(\frac{\partial\sigma}{\partial \ln a_\pm}\right)_{\varphi^+} \tag{1}$$

at various potentials for 0.3, 1.8, 4.45, 6.6, and 8.45 N $NaClO_4$. (In Eq. (1), R is the gas constant, T the absolute temperature, and $a_\pm$ the mean activity of the electrolyte.) The charge densities of the mercury surface were obtained by numerical integration of the differential capacity curves in the same solutions (see [1]), and consequently the connection between charge density ε and potential φ^+ was established. This made it possible to represent the Γ_- values found as a function of electrode charge. The data thus obtained are shown in Fig. 1.

At the same time we present in Fig. 1 Γ_- values obtained for 0.3 and 1.8 N $NaClO_4$ by simultaneous solution of the equations

$$\Gamma_+ + \Gamma_- = -\frac{1}{RT}\left(\frac{\partial\sigma}{\partial \ln a_\pm}\right)_{\varphi} \tag{2}$$

and

$$\Gamma_+ - \Gamma_- = -\varepsilon / F. \tag{3}$$

* Sodium amalgams were prepared by electrolysis of a NaOH solution purified by prolonged cathodic polarization above a mercury electrode.

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TABLE 1

φ, V (sce)	c_0					
	0.1 N	1,0 *N*	3,3 *N*	5,5 *N*	7,65 *N*	9,2 *N*
+0,3	344,6	334,9	328,4	327,0	324,8	320,7
+0,2	364,9	356,0	349,2	346,8	344,7	342,0
+0,1	381,4	372,9	366,0	363,0	360,9	359,8
0,0	394,7	387,0	380,8	377,6	376,5	374,2
—0,1	404,9	399,2	393,0	391,0	389,8	386,8
—0,2	413,3	409,0	404,0	402,0	399,5	397,9
—0,3	420,6	416,8	411,4	409,6	408,8	407,6
—0,4	424,2	421,0	417,0	415,8	415,2	414,2
—0,5	425,0	422,8	420,4	418,6	418,5	418,6
—0,6	423,2	421,5	420,0	419,0	420,3	420,3
—0,7	419,2	417,6	417,0	417,0	418,6	420,0
—0,8	412,8	410,7	411,2	411,2	414,5	417,6
—0,9	404,7	402,2	403,2	403,6	407,7	411,0
—1,0	394,8	391,4	392,8	393,9	397,6	401,5
—1,1	382,8	378,8	380,2	381,8	386,8	390,2
—1,2	369,6	364,8	365,8	367,8	372,1	376,9
—1,3	355,0	349,5	349,6	351,5	356,3	359,8
—1,4	339,0	332,5	332,3	333,0	337,7	340,7
—1,5	320,8	313,4	312,0	313,0	316,9	319,5
—1,6	300,9	292,4	290,0	290,0	293,3	296,2
φ_{am}	—2,154	—2,105	—2,070	—2,046	—2,035	—2,023

where Γ_+ is the Gibbs surface excess of the cations and F is Faraday's number. In Eq. (2) the derivative $\partial\sigma/\partial \ln a_\pm$ is taken at constant potential as measured against sce.

Figure 1 shows that the data obtained by the two methods for not very concentrated $NaClO_4$ solutions agree well with each other, which indicates that the φ^+ values found by us are correct. In more concentrated solutions, however, the notion that the potential φ remains constant when varying the salt concentration becomes unfounded [4], and the second method of calculating the Gibbs surface excesses proves inapplicable.

Since Eq. (3) remains valid for all electrolyte concentrations, we can readily obtain from the data given in Fig. 1 the Gibbs surface excess of the sodium ions in the corresponding solutions as function of charge density on the mercury surface. Such data for the negatively charged surface are presented in Fig. 2. From this it is seen that in

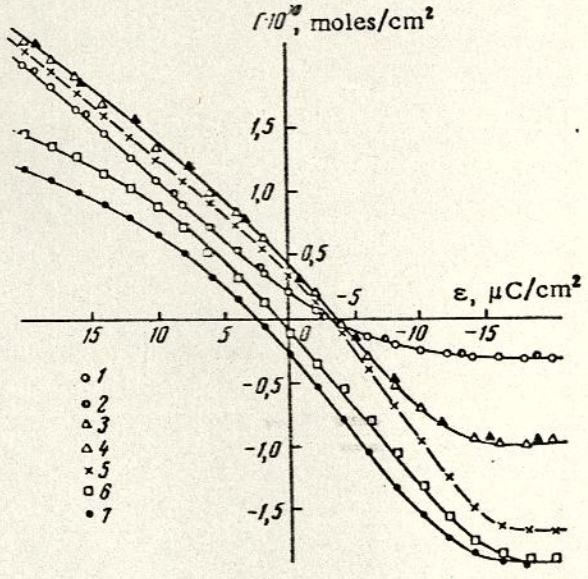

Fig. 1. The Gibbs surface excess of ClO_4^- ions as function of charge density of a mercury electrode at the following $NaClO_4$ concentrations: 1) 0.3; 3) 1.8; 5) 4.45; 6) 6.6; 7) 8.45 N; 2, 4) are data for 0.3 and 1.8 N $NaClO_4$ obtained with the aid of Eqs. (2) and (3).

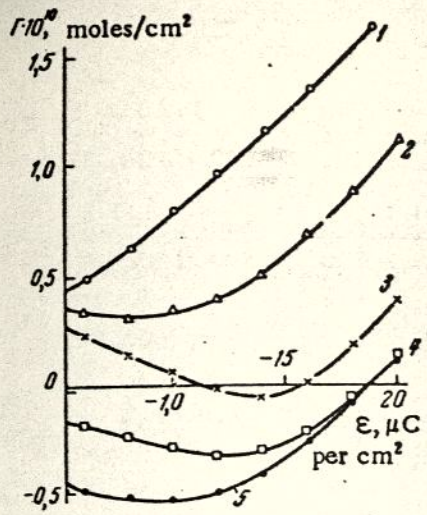

Fig. 2. The Gibbs surface excess of Na^+ ions as function of charge density on the mercury electrode at the following $NaClO_4$ concentrations: 1) 0.3; 2) 1.8; 3) 4.45; 4) 6.6; and 5) 8.45 N.

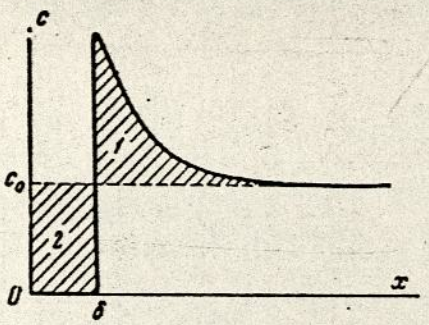

Fig. 3. Schematic dependence of the ionic concentration on the distance from the electrode in presence of a layer of adsorbed water molecules on the electrode surface that is impermeable for ions.

highly concentrated $NaClO_4$ solutions at $\varepsilon < 0$, in spite of the electrostatic attraction of the cations, we have $\Gamma_+ < 0$. A similar effect was noted by Iofa and Frumkin [3] for the adsorption of H_3O^+ ion on mercury from highly concentrated HCl and H_2SO_4 solutions.

From a physical point of view, negative adsorption occurs because there exists an interlayer of solvent molecules possessing a low dielectric constant between the mercury surface and the adsorbing ions [5]. In fact, in presence of this kind of interlayer the distribution of cations in the electric double layer at $\varepsilon < 0$ can schematically be represented by the curve shown in Fig. 3. The Gibbs adsorption represents the surface excess of ions; therefore, the sign of the quantity Γ is determined by the relative sizes of the shaded areas on Fig. 3, i.e., $\Gamma = S_1 - S_2$. Thus, if $S_1 < S_2$, then $\Gamma < 0$. Negative adsorption of Na^+ ions at $\varepsilon < 0$ indicates, therefore, that even in highly concentrated $NaClO_4$ solutions there is an interlayer of water molecules between the ions of the double layer and the mercury surface.

The dependence of negative adsorption on electrolyte concentration allows the thickness of this interlayer (δ) to be evaluated under the assumption that it is entirely impermeable for the ions of the solution [6-8]. If at the potential of zero charge (pzc) specific adsorption of ions is absent, then the δ value found in this way does not depend on any model of the diffuse layer. Thus, in [7] it was established that at the pzc in K_2CO_3, $MgSO_4$, and $MnSO_4$ solutions the mean value of $\delta \approx 3.3$ A. Unfortunately the specific adsorption of ClO_4^- ions infringes on this condition in the case of $NaClO_4$ solutions. It seems that at sufficiently large negative surface charge densities ($|\varepsilon| \geq 15$ $\mu C/cm^2$), one can neglect the specific adsorption of ClO_4^- ions; however, one must then make certain assumptions about the distribution of ions in the diffuse layer.

Parsons and Zobel suggested [8] that the distribution of ions in the diffuse layer obeys the classical Gouy-Chapman-Grahame theory [9]. In this case δ is determined by the slope of the plot of $-(\Gamma_- - \Gamma_-^{el})$ against salt concentration, where the electrostatic adsorption of anions (Γ_-^{el}) is evaluated with the formula [7]

$$F\Gamma_{-\,el} = \frac{\varepsilon}{2} + \sqrt{\frac{DRTc_0}{2\pi} + \frac{\varepsilon^2}{4}} - \sqrt{\frac{DRTc_0}{2\pi}} = \frac{\varepsilon}{2} + \frac{1}{2}\sqrt{137.8c_0 + \varepsilon^2} - 5.87\sqrt{c_0}, \qquad (4)$$

where D is the dielectric constant in the diffuse layer and c_0 is the bulk concentration of the 1,1-valent electrolyte. The numerical factors hold for a temperature of 25°C under the condition that $F\Gamma_-^{el}$ and ε are expressed in $\mu C/cm^2$, and c_0 in mole/liter. Plots of $-(\Gamma_- - \Gamma_-^{el})$ against $NaClO_4$ concentration derived in this way for two charge densities on the electrode, $\varepsilon = -15$ $\mu C/cm^2$ and $\varepsilon = -19$ $\mu C/cm^2$, are shown in Fig. 4. The data for these two charge densities fall practically on one curve having an initial slope corresponding to $\delta \approx 3$ A, in agreement with the data of [7] and [8]. However, Fig. 4 shows also that at higher $NaClO_4$ concentrations the slope of the plot of $-(\Gamma_- - \Gamma_-^{el})$ against c_0 decreases, corresponding to $\delta \approx 1.5$ A at $c_0 = 8.45$ N.

One of the possible explanations for this effect is partial dehydration of the Na^+ ions, and the effect can be linked, therefore, with the notable rise in double layer capacity at negative surface charges in highly concentrated solutions [1, 10, 11]. On the other hand, the deviation of the concentration dependence of $-(\Gamma_- - \Gamma_-^{el})$ from a straight line can be explained by substantial errors in the calculated values of Γ_-^{el} since in highly concentrated electrolyte solutions the classical diffuse layer theory ceases to apply.

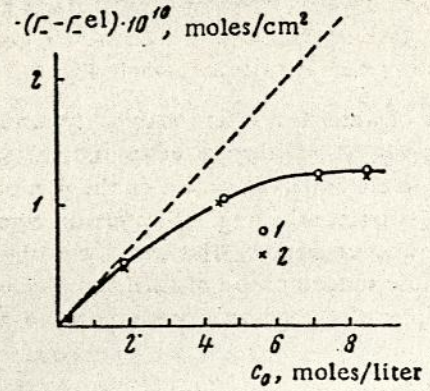

Fig. 4

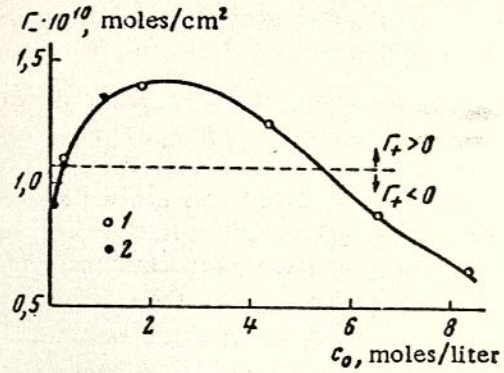

Fig. 5

Fig. 4. Dependence of $-(\Gamma_- - \Gamma_-^{el})$ on $NaClO_4$ concentration at the following charge densities of a mercury electrode: 1) $\varepsilon = -15\ \mu C/cm^2$; 2) $\varepsilon = -19\ \mu C\ cm^2$.

Fig. 5. The Gibbs surface excess of ClO_4^- ions as a function of $NaClO_4$ concentration at $\varepsilon = +10\ \mu C/cm^2$: 1) data obtained in the present work; 2) data from [13].

In fact, if we neglect the diffuseness of the double layer in highly concentrated solutions, then the negative surface charge must be compensated in full by adsorbed Na^+ ions whose amount is determined by the area S_1 in Fig. 3, i.e., $S_1 = -\varepsilon/F$. If the surface excess of cations $\Gamma_+ = 0$, then under these conditions $S_1 = S_2 = c_0\delta$ and, consequently,

$$\delta = -\varepsilon / c_0 F. \qquad (5)$$

A calculation of the thickness of the aqueous interlayer according to this formula for the intersections of the $\Gamma_+ - \varepsilon$ curves with the abscissa (see Fig. 2) gives $\delta = 3.7$ A for $c_0 = 4.45$ N, $\delta = 2.9$ A for $c_0 = 6.6$ N, and $\delta = 2.3$ A for $c_0 = 8.45$ N. It follows that if the diffuseness of the double layer in highly concentrated $NaClO_4$ solutions is neglected, the δ values then calculated are even closer to those obtained in more dilute solutions, allowing for the classical distribution of ions in the diffuse layer. It can be suggested, therefore, that with increasing $NaClO_4$ concentration a gradual transition occurs from the classical diffuse double layer [9] to a compact structure corresponding to Helmholtz' theory [12]. Since during such a transition one must also expect a certain rise in double layer capacity, it appears that the effect of partial dehydration of the cations is not the sole cause for the rise in differential capacity at $\varepsilon < 0$ in highly concentrated solutions.

Figure 1 shows that at positive charges of the mercury surface, the plot of the Gibbs surface excess of ClO_4^- ions against $NaClO_4$ concentration goes through a maximum. For $\varepsilon = +10\ \mu C/cm^2$, this dependence is shown in Fig. 5. Along with our data, Fig. 5 also gives Γ_- values obtained by Bockris and coworkers [13] for the more dilute $NaClO_4$ solutions.* The figure shows that over the range of $NaClO_4$ concentrations where the data overlap, very good agreement between the various authors is observed.

It follows from Eq. (3) and the data presented in Fig. 5 that the adsorption of cations at $\varepsilon > 0$ also goes through a maximum, with $\Gamma_+ < 0$ at low and at very high $NaClO_4$ concentrations. The dotted line in Fig. 5 shows the regions of positive and negative Gibbs adsorption of cations at $\varepsilon = +10\ \mu C/cm^2$.

The reduction in Gibbs surface excess of ClO_4^- ions with rising $NaClO_4$ concentration at positive surface charges leads to the conclusion that between the mercury surface and the perchlorate ions adsorbed on it there exists an interlayer of water molecules. Thus, the specific adsorption of ClO_4^- ions (and apparently that of other, similar anions: NO_3^-, PF_6^-, BF_4^-, and CF_3COO^-) is not accompanied by their dehydration on the side towards the mercury surface. This may be due to the fact that the superequivalent adsorption of these ions is caused, not by covalent forces of interaction with the mercury surface, but by an effect of "squeezing-out" from the bulk solution [14]. In

* In [13] tabulated data for the specifically adsorbed charge of anions (ε_1) at various charge densities of the electrode, ε, are given. Since the ε_1 in [13] were calculated on the basis of the experimental values for ε_1 and ε with the aid of Grahame's theory [9], the reverse calculation of the Gibbs surface excess from the ε_1 and ε data is not difficult. In fact, the total diffuse layer charge $\varepsilon_2 = -\varepsilon - \varepsilon_1$; the diffuse layer charge due to anions, ε_2^-, is determined from Eq. (4), substituting in it $F\Gamma_-^{el}$ by $-\varepsilon_2^-$ and the electrode charge ε by $-\varepsilon_2$; and finally $\Gamma_- = -(\varepsilon_1 + \varepsilon_2^-)/F$.

fact, if there is on the mercury surface a sufficiently tightly bound layer of water molecules, then further "squeezing-out" is precluded when the ClO_4^- ions come in contact with this layer. Therefore, the distribution of perchlorate ions at the positively charged mercury surface can also be represented schematically as shown in Fig. 3.

At medium concentrations of $NaClO_4$, while the structure of water is not yet too strongly disturbed by the ClO_4^- ions, the "squeezing-out" effect leads to $S_1 > S_2$ and, moreover, with increasing salt concentration S_1 grows more rapidly than $S_2 = \delta c_0$. Since $\Gamma_- = S_1 - S_2$, one observes under these conditions an ascent on the plot of Γ_- against c_0 (see Fig. 5). On the other hand, in highly concentrated $NaClO_4$ solutions the original water structure is practically destroyed and the "squeezing-out" effect is, therefore, substantially weakened. This causes now the area S_2 to grow faster than S_1 with increasing $NaClO_4$ concentration, and the Gibbs surface excess of ClO_4^- ions decreases as a consequence (Fig. 5). It is readily seen that the maximum on the plot of Γ_- against c_0 corresponds to the condition $dS_1/dc_0 = \delta$.

The existence of an interlayer of water molecules between the mercury and the ClO_4^- ions adsorbed on it makes it possible to explain the low capacity values in perchlorate solutions at positive surface charges (see, for example, [1]), the expulsion of ClO_4^- ions by F^- ions at large positive charge densities of the mercury electrode [15], as well as the fact that the theory of the "hump" on differential capacity curves, which is based on the concept of reorientation of adsorbed water dipoles, agrees best with the experimental data in solutions of perchlorates or salts with similar anions [16]. Besides, the possibility is not excluded that the concepts concerning the adsorption of ClO_4^- ions on mercury put forward here will help explain the anomalous behavior of these ions on the interface of a gallium electrode with aqueous perchlorate solutions [17].

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