DIFFERENTIAL CAPACITANCE CURVES OF A MERCURY ELECTRODE FOR CONCENTRATED SOLUTIONS OF SALTS IN METHANOL AND ETHANOL

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The laws governing the curves of the differential capacitance of a mercury electrode in concentrated aqueous solutions of various salts were investigated in [1-5]. It seemed of interest to study the analogous laws for concentrated solutions in solvents other than water.

The limited solubility of salts in nonaqueous solvents curtails the number of possible objects for this study. In order to obtain the highest possible salt concentrations we chose solutions of $Ca(ClO_4)_2$ in methanol and ethanol and solutions of $SrBr_2$ in CH_3OH.

The reagents were purified and the solutions were prepared in the following way. The salt $Ca(ClO_4)_2$ was prepared from specially purified $CaCO_3$ and with distilled $HClO_4$. $SrBr_2$ was prepared by double recrystallization. The water was extracted from the salts in vacuo at 200°C. Ethyl and methyl alcohol were dried by $CuSO_4$, CaO, and metallic calcium in succession. Pure hydrogen was saturated by the vapor of the solvent from the solution of which the concentration was to be investigated and then bubbled through the solutions in a cell.

The differential capacitance C of a mercury drop electrode was measured by means of an impedance bridge [3] with an ac frequency of 400 c. All the measurements relate to a temperature of 20°C. The potential φ of the mercury electrode was measured in reference to a water-saturated calomel half-cell connected to the test solution through a phial with saturated KCl in water. The zero-charge potential φ_0 of the mercury electrode in the systems investigated was also measured by means of the same circuit. The correctness of the φ_0 value found in this way was checked by the agreement between the potential of an open flowing electrode and the τ-maximum potential of the φ curve, where τ is the drop period of the mercury electrode*. Then, the surface charge ε was determined by numerical integration of the formula $\varepsilon = \int_{\varphi_0}^{\varphi} C\, d\varphi$ and the measured C values were plotted versus the calculated values of ε. This method of evaluating the experimental data made it possible, as in the case of concentrated aqueous solutions [3, 4], to avoid inaccuracies due to the unknown dependence of the interphase potential on the salt concentration.

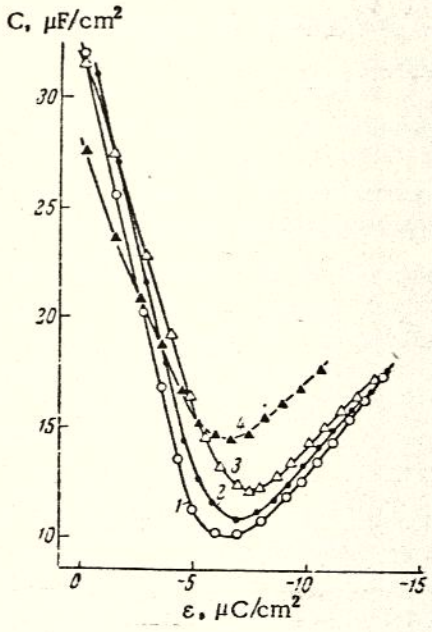

Fig. 1. Curves of the differential capacitance of a mercury electrode for $SrBr_2$ solutions in methanol. $SrBr_2$ concentrations: 1) 1, 2) 2, 3) 4, 4) 6 N.

The results obtained in the form of C-versus-ε curves for various concentrations are shown in Figs. 1-3. It is clear from these figures that the minimum differential capacitance at $\varepsilon < 0$ increases considerably in highly concetrated alcoholic solutions as in the case when water is used as a solvent [1-5]. In the same way as for

* The φ_0 of the investigated systems were determined by L. M. Roshchupkina and V. F. Khonina to whom we express our sincere gratitude.

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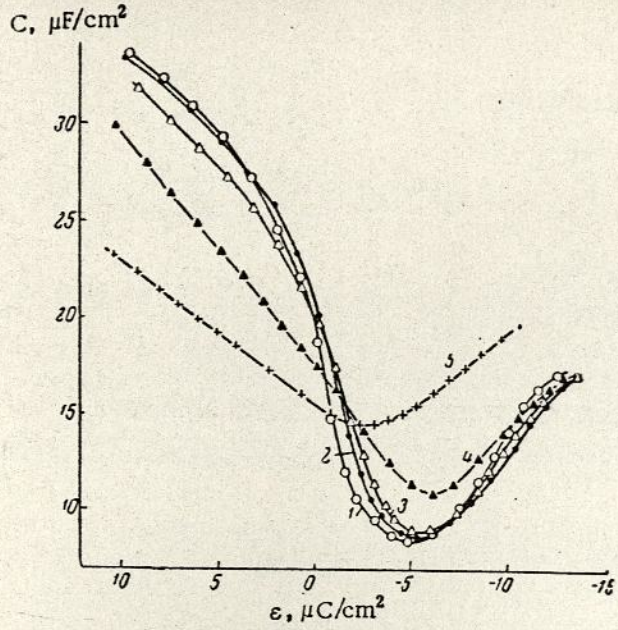

Fig. 2. Curves of the differential capacitance of a mercury electrode for $Ca(ClO_4)_2$ solutions in methanol. Ca $(ClO_4)_2$ concentration: 1) 1, 2) 2, 3) 4, 4) 6, and 5) 9.5 N.

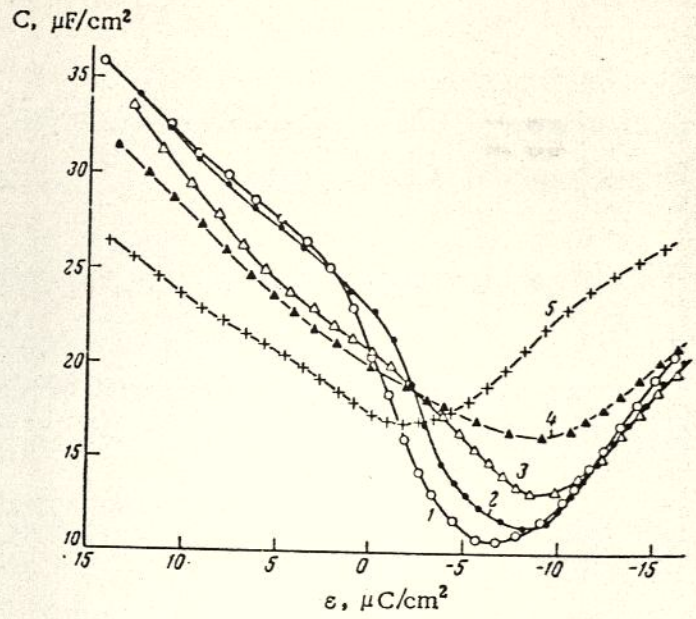

Fig. 3. Curves of the differential capacitance of a mercury electrode for $Ca(ClO_4)_2$ solutions in ehtanol. Ca $(ClO_4)_2$ concentration: 1) 0.1, 2) 1, 3) 2, 4) 4, and 5) 7.6 N.

concentrated aqueous solutions this phenomenon can be related to two effects: 1) a partial dissolution of the adsorbed cations [2, 3] and 2) the pulling of anions into the electric double layer and the gradual transition to a stratified structure of melts [4, 6]. These two effects are obviously interconnected because the cations and anions, which are the basis of the second effect, undergo a partial or complete dissolution before interacting.

Since the first effect is weaker with sufficiently high negative charges of the electrode than when ε is less negative* it can be expected that, as a result of the first effect, the minimum of the C-versus-ε curves is shifted to more negative ε values when the salt concentration increases. As is evident from Figs. 1-3, this assumption is right for a certain range of concentrations. For very high salt concentrations, however, there is a considerable shift in the minimum of the C-versus-ε curves to the positive side and a corresponding increase in capacitance with high negative surface charges. Under such conditions, the C-versus-ε curves become more symmetrical, and their minimum approaches $\varepsilon = 0$. This is particularly clear in the case of $Ca(ClO_4)_2$ solutions (Figs. 2 and 3).

Since such a behavior is characteristic of the differential capacitance curves measured with melts of salts [7], it can be assumed that the shift of the minimum of the C-versus-ε curves towards less negative values of ε indicates that the association of ions begins to take over a decisive part in the process of rearrangement of the electric double layer, which finally leads to the stratified structure of the melts [8]. This is confirmed by the fact that the salt concentration at which this effect can be observed decreases on transition from $Ca(ClO_4)_2$ to $SrBr_2$ (Figs. 1 and 2) and on transition from CH_3OH to C_2H_5OH (Figs. 2 and 3), i. e., when conditions are more favorable to the formation of ion pairs.

The characteristic maximum (hump) appearing on the C-versus-ε curves (see, e. g., [3]) interferes with the observation of the above behavior in the case of aqueous solutions. In the case of alcoholic solutions there is no such hump on the C-versus-ε curves, none in the case of bromides nor in the case of perchlorates of any concentration. The circumstance has a special significance. If it is assumed, according to the theory of Bockris, Devanathan, and Müller [9], that the hump in the differential capacitance curves is determined completely by the laws of anion adsorption then it should be expected to appear on the C-versus-ε curves in concentrated alcoholic solutions as it was observed in concentrated aqueous solutions of liquid gallium electrode [10]. The absence of this effect found by us is therefore another argument in favor of the theories of the hump based on the reorientation of the adsorbed solvent dipoles [11, 12].

* At sufficiently negative ε a partial desolvation of the cations also takes place in diluted solutions because of electrostatic attraction.

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