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CAPACITANCE OF THE ELECTRIC DOUBLE LAYER IN N-METHYLFORMAMIDE

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The capacitance of the double layer in nonaqueous solvents has been studied in a number of works ($^{1-6}$). In the cited works, aliphatic alcohols were used as solvents, whose dielectric constant is appreciably lower than that of water. This, apparently, could explain the decrease in the capacitance of the double layer on going from aqueous solutions to alcoholic ones (^{1}, ^{3}, ^{4}). Another feature of the dependence of the differential capacitance (C) on the electrode potential (φ) in solutions of aliphatic alcohols is the absence of the characteristic hump which, in aqueous solutions, is observed near the point of zero charge (p.z.c.). According to (^{7}), the hump on the $C-\varphi$ curves is due to a maximum in the effective dielectric constant of the layer of adsorbed solvent dipoles, and its absence in solutions of CH_3OH or C_2H_5OH may be connected either with a stronger orientation of alcohol molecules on the mercury surface, which changes only slightly under the action of the field of the double layer, or with the lower freezing temperatures of the alcohols; therefore, capacitance data in CH_3OH and C_2H_5OH at 25° should be compared with $C-\varphi$ curves measured in water at a higher temperature (^{1}, ^{8}).

In the present work, $C-\varphi$ curves were measured by the impedance-bridge method (^{9}) on a mercury dropping electrode in solutions of various salts in N-methylformamide, whose dielectric constant is appreciably greater than that of water ($D = 182.4$ (^{10})). Potentials are given relative to a normal calomel electrode connected to the cell through a cup containing a saturated solution of KCl in water. Commercial $HCONHCH_3$ was twice distilled in vacuum (~ 1 mm Hg), then treated with CaO and distilled in vacuum. The latter operation was repeated twice. After this, $HCONHCH_3$ was distilled under reduced pressure in a nitrogen atmosphere through a rectification column. The N-methylformamide thus obtained had a specific electrical conductivity of $2\text{-}4 \cdot 10^{-7}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$ at 20°, a freezing temperature of $-3.4°$, and a refractive index $n_D^{20} = 1.4300$. Before the capacitance measurements, the prepared solutions were subjected to cathodic polarization on mercury in a hydrogen atmosphere with a current of $1\text{-}6 \cdot 10^{-5}\ \mathrm{A/cm^2}$ for 20 hr.

The data obtained are shown in Figs. 1-4*. As is evident from the figures, the capacitance of the double layer in N-methylformamide is, in general, smaller than in water. Thus, in 0.1 N KCl at $\varphi = -1.8$ V, $C = 8.8\ \mu\mathrm{F/cm^2}$, and at $\varphi = -0.6$ V, $C = 13.9\ \mu\mathrm{F/cm^2}$. Since the p.z.c. in this solution is -0.41 V**, the

Fig. 1. Curves of differential capacitance in N-methylformamide at 25° in 0.1 N solutions: 1 –KCl, 2 –KBr, 3 –KI, 4 –RbCl, 5 –CsCl, 6 –NaCl, 7 –LiCl

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noted potentials correspond to a negatively charged mercury surface. Therefore, one of the reasons for the decrease in capacitance in comparison with aqueous solutions may be an increase in the radius of the solvated cation on going from H_2O to $HCONHCH_3$. On the other hand, the small values of the double-layer capacitance in N-methylformamide solutions indicate a substantially smaller value of the effective dielectric constant in the surface layer than in the bulk of the solution ([11]).

With positive charges of the surface, a sharp rise is observed capacitance, associated with specific adsorption of Cl^- anions. As in the case of aqueous solutions(12), the adsorbability of anions increases in the series: $Cl^- < Br^- < I^-$, and the ascending branch of the $C—\varphi$ curve is shifted toward more negative potentials (Fig. 1). In the presence of the Cs^+ cation, a similar rise in the $C—\varphi$ curve is observed at strongly negative polarizations, which indicates a noticeably greater superequivalent adsorption at negative potentials from $HCONHCH_3$ solutions than from aqueous solutions(13). The Rb^+ cation, in its adsorbability on mercury from N-methylformamide solutions, occupies an intermediate position between K^+ and Cs^+, approaching the potassium cation in its properties. In the series K^+–Na^+–Li^+, a slight increase in capacitance is observed at potentials more negative than −1.2 V and a slight decrease in it in the region of the maximum on the $C—\varphi$ curve (Fig. 1). This phenomenon, which occurs neither in aqueous(13,14) nor in alcoholic(4,5) solutions, requires further investigation.

Fig. 1. Curves of differential capacitance in N-methylformamide at 25° in 0.1 *N* solutions: 1 –KCl, 2 –KBr, 3 –KI, 4 –RbCl, 5 –CsCl, 6 –NaCl, 7 –LiCl

Upon dilution of the solutions, the double layer becomes more diffuse and the capacitance near the p.z.c. decreases (Fig. 2a). However, the decrease in capacitance in N-methylformamide solutions is noticeably smaller than in water at the same electrolyte concentrations. This result is due to the fact that the

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* The capacitance of the double layer over the entire investigated potential range does not depend on the frequency of the alternating current, which we varied from 400 to 10,000 Hz. The data presented were obtained at a frequency of 400 Hz.

** The p.z.c. was determined from the maximum of the electrocapillary curve in a 0.1 *N* KCl solution in N-methylformamide.

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

capacitance of the compact layer (C_{g}) in N-methylformamide is smaller than in water, whereas the capacitance of the diffuse layer (C_{d}) is larger (owing to the higher dielectric constant). Therefore, when C_{g} and C_{d} are connected in series, the capacitance of the diffuse layer, which is a function of concentration, has a smaller influence on the total differential capacitance in N-methylformamide than in water.

A characteristic feature of the C—φ curves in N-methylformamide is the presence of a maximum (hump) at potentials of −0.95—1.05 V. The temperature dependence of the capacitance at the maximum on the C—φ curve, pri-

shown in Fig. 3*, makes it possible to suppose that the hump on the capacitance curves in solutions of $HCONHCH_3$ has the same nature as in the case of aqueous solutions, i.e., it is associated with a change in the orientation of the solvent dipoles (^{15}).

Fig. 2. Curves of differential capacitance in N-methylformamide at 25°. **a** –in KCl solutions: 1 –0.1 N, 2 –0.03 N, 3 –0.01 N; **b** –in solutions: 1 –0.1 N NaCl, 2 –0.1 N NaCl + 10^{-3} N $[(C_4H_9)_4N]$Br.

Fig. 3. Curves of differential capacitance in 0.1 N KCl in N-methylformamide at temperatures: 1 –0°, 2 –25°, 3 –50°.

* At $t > 50^{\circ}$ $HCONHCH_3$ begins to decompose noticeably, which did not allow us to carry out capacitance measurements at higher temperatures.

The significantly smaller temperature coefficient of capacitance in N-methylformamide compared with aqueous solutions (^{8,15}) can be explained by the stronger adsorption of $HCONHCH_3$ dipoles on the mercury surface. This conclusion is supported by the low value of the surface tension at the boundary in N-methylformamide solutions (in 0.1 N KCl $\sigma_{\mathrm{max}} = 382.0$ dyn/cm), as well as by the capacitance data obtained by us in a solution of 0.1 N NaCl + 10^{-3} N $[(C_4H_9)_4N]$Br (Fig. 2b). In the latter case, as can be seen from Fig. 2b, $HCONHCH_3$ molecules strongly bound to the surface hinder the adsorption on mercury of the cations $[(C_4H_9)_4N]^+$, in the presence of which, as is known (^{6,16}), the capacitance of the double layer decreases to 4-5 μF/cm^2.

Since the hump on the C-φ curves in N-methylformamide solutions corresponds to negative surface charges, and since $HCONHCH_3$ molecules are strongly adsorbed on the mercury surface, the influence of specific adsorption on the orientation of solvent dipoles (^{15}) in the potential region of the hump may be

Fig. 4. Differential-capacitance curves in 0.1 N KCl in mixtures of water and N-methylformamide at 25°, addition of N-methylformamide (in mol. %): 1 –0, 2 –3.3, 3 –11.6, 4 –31.4, 5 –100

Figure 4: Fig. 4. Differential-capacitance curves in 0.1 N KCl in mixtures of water and N-methylformamide at 25°, addition of N-methylformamide (in mol. %): 1 –0, 2 –3.3, 3 –11.6, 4 –31.4, 5 –100

neglected. Thus, developing the concepts of work (7), it may be assumed that the hump on the C-φ curves in N-methylformamide solutions is due to a maximum in the effective dielectric constant of the layer of adsorbed $HCONHCH_3$ molecules. However, in the present case the minimum dielectric saturation does not correspond to the p.z.c., which can be explained by the predominant orientation of $HCONHCH_3$ molecules at the p.z.c., in which the negative end of the dipole

oriented toward the surface of the mercury. With such an explanation, the hump on the $C - \varphi$ curves should practically not depend on the nature of the electrolyte, which is in agreement with the experimental data shown in Fig. 1.

Small additions of water to N-methylformamide solutions practically do not change the shape of the $C - \varphi$ curve. At a high water content, destruction of the layer of adsorbed $HCONHCH_3$ molecules occurs, which leads to a decrease of the hump on the $C - \varphi$ curves (as also upon increasing the temperature), and also to an increase in capacitance at more negative potentials owing to a decrease in the thickness of the double layer during adsorption of hydrated cations (6) (Fig. 4). On the other hand, even small additions of N-methylformamide to aqueous solutions, owing to its strong adsorbability on the mercury surface, destroy the layer of adsorbed water dipoles, which leads to the complete disappearance of the hump on the $C - \varphi$ curves in aqueous solutions, just as occurs upon increasing the temperature (8,15).

Fig. 4. Differential-capacitance curves in 0.1 *N* KCl in mixtures of water and N-methylformamide at 25°, addition of N-methylformamide (in mol. %):
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