SPECIFIC ADSORPTION OF TETRAALKYLAMMONIUM IONS ON BISMUTH FROM NONAQUEOUS SOLVENTS

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A procedure for the calculation of the characteristics of the inner part of the electrical double layer has been elaborated on the basis of the capacity data obtained in the conditions of specific adsorption of ions, accompanied by an increase of the inner layer dimensions. The formulae derived have been verified by studying the specific adsorption of tetraalkylammonium cations from aliphatic alcohols.

In the theory of the "metal/solution" interface the development of the quantitative relationships of the inner part of double layer has a fundamental importance. The inner layer structure significantly depends on the nature of electrode material and of solvent, on specific adsorption of ions and molecules, on their chemical nature, geometrical configuration and dimensions. In adsorption of simple inorganic ions the variation of the inner layer dimensions can be neglected because of the comparatively low coverages of the electrode surface and small dimensions of the ions adsorbed. However, if the inner layer thickness considerably increases as a result of the specific adsorption, the inner layer capacity can decrease and this effect leads to serious distortions of the adsorption parameters, unless special models are used for the calculations. Typical representatives of such systems are mixed solutions of tetraalkylammonium ions (TAA) and of inorganic reference ions of constant ionic strength.

In this paper the procedure has been elaborated and experimentally verified for the calculation of the inner layer parameters in the conditions, where specific adsorption of ions is accompanied by a remarkable increase of the inner layer thickness. To minimize the calculation inaccuracy and to simplify the analysis of the experimental data the systems have been chosen, where the specific adsorption is not accompanied by the change of the inner layer dielectric properties and the quantitative treatment of the experimental results can be accomplished by simple calculation methods, for example, by the Hurwitz–Parsons–Dutkiewicz method[1,2]. In the first approximation these conditions are fulfilled in the adsorption of the TAA cations from the alcoholic solvents if the hydrocarbon radicals of the solvent molecule and of the TAA ion studied are similar as to their chemical nature and geometry. The main conditions of the applicability of the Hurwitz–Parsons–Dutkiewicz method are satisfied if relatively low ionic strengths of the solutions and suitable reference ions are used. Variation of the chemical nature of the surface-active ions and of the solvent enables to vary the inner layer thickness in the adsorption process.

EXPERIMENTAL

The adsorption of TAA cations was carried out from the following systems: *1*) 0·005 mM-$N(CH_3)_4$.ClO_4 + 0·005(1 − *m*)M-$LiClO_4$ in methanol; *2*) 0·01 mM-$N(C_2H_5)_4ClO_4$ + 0·01(1 − *m*)M-$LiClO_4$ in ethanol; *3*) 0·01 mM-$N(C_4H_9)_4ClO_4$ + 0·01(1 − *m*)M-$LiClO_4$ in ethanol). As will be shown the adsorption of the TAA cations from alcohols may cause the recharge of the electrode surface at sufficiently high negative surface charge densities[3,4]. In this case the errors due to the different dimensions of the reference ions and the ions of TAA are relatively small[5]. The analysis shows that the surface concentrations of TAA ions can be estimated in the precision limits of 3—7% (depending on the system) when considering the main sources of the errors (differences in the ionic radii, in the activity coefficients and in the association constants of the reference electrolyte and of TAA salts). For comparison the adsorption of tetrabutylammonium cations was studied from aqueous solutions.

The experimental data have been obtained by measuring the dependence of the differential capacity *C* of a solid bismuth electrode on its potential *E* in alcoholic solutions at 25°C. The equilibrium capacities have been determined by the extrapolation of the frequency dispersion of the capacity to zero frequency. The electrodes have been prepared in a special device described previously[6]. The TAA salts have been prepared by neutralization of TAA hydroxides with $HClO_4$. The salts were purified by a multiple recrystallization from methanol or ethanol. The standard procedures have been used for purification and removal of the small residues of water (boiling on calcium oxide, treatment with metallic magnesium and fractional destillation[7]).

RESULTS

In Figs 1 and 2 the sets of capacity curves (*C*,*E*-curves) are represented for two systems studied. As seen in these figures the curves significantly differ from those for aqueous

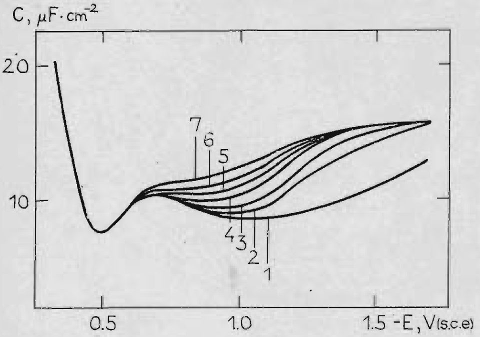

FIG. 1

Differential capacity curves of bismuth electrode in methanolic solutions for the system 0·005 mM-$N(CH_3)_4ClO_4$ + 0·005 (1 − *m*) M-$LiClO_4$ for *m*: *1* 0; *2* 0·02; *3* 0·05; *4* 0·1; *5* 0·2; *6* 0·5; *7* 1·0

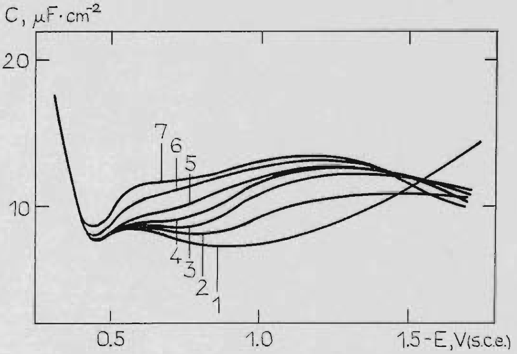

FIG. 2

Differential capacity curves of bismuth electrode in ethanolic solutions for the system 0·01 mM-$N(C_2H_5)_4ClO_4$ + 0·01 (1 − *m*) M-$LiClO_4$ for *m*: *1* 0; *2* 0·02; *3* 0·05; *4* 0·1; *5* 0·2; *6* 0·5; *7* 1·0 solutions of the TAA salts (Fig. 3) and for ethanolic solutions of the surface-active inorganic salts (Fig. 4). As will be shown below, the shape of the capacity curves in Fig. 1 and 2 is due to the superposition of the two following effects: *a*) the capacity increase due to the specific adsorption of TAA cations; *b*) the capacity decrease due to the increase of the inner layer dimensions (the distance of the outer Helmholtz plane x_2 from the electrode surface) caused by the entrance of the large TAA cations into the inner layer.

On the basis of the capacity data the charge of the specifically adsorbed TAA cations q_1^+ has been calculated using the Hurwitz–Parsons–Dutkiewicz method. The plots of q_1^+ against the electrode charge density q are shown in Fig. 5 and 6 for the $N(CH_3)_4^+$ and $N(C_2H_5)_4^+$ cations. The data obtained indicate that the TAA cations adsorb from alcohols considerably stronger than the inorganic cations (Cs^+, K^+, ref.[8,9]) and at high $-q$ they lead to the recharge of the electrode surface.

The following procedure has been elaborated to consider the increase of the effective dimensions of the inner layer due to the specific adsorption of the TAA

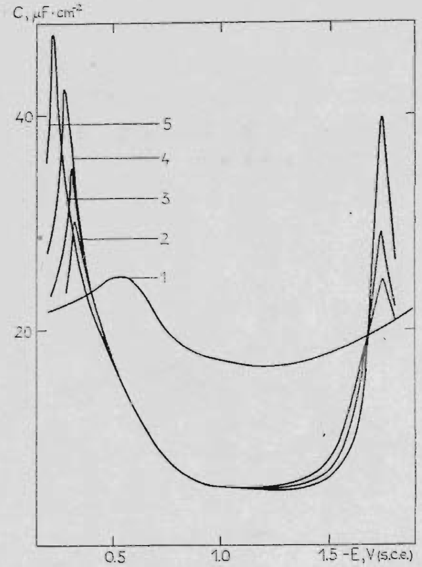

FIG. 3

Differential capacity curves of bismuth electrode in aqueous solutions for the system $0{\cdot}1\text{M-LiClO}_4 + c\text{M-N(C}_4\text{H}_9)_4\text{ClO}_4$ for *c*: *1* 0; *2* 10^{-4}; *3* $2 . 10^{-4}$; *4* $5 . 10^{-4}$; *5* 10^{-3}

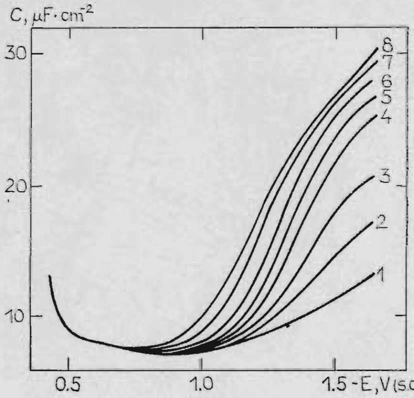

FIG. 4

Differential capacity curves of bismuth electrode in ethanolic solutions of the system $0{\cdot}01\ \text{mM-CsCl} + 0{\cdot}01(1 - m)\ \text{M-LiCl}$ for *m*: *1* 0; *2* 0·01; *3* 0·02; *4* 0·05; *5* 0·1; *6* 0·2; *7* 0·5; *8* 1·0

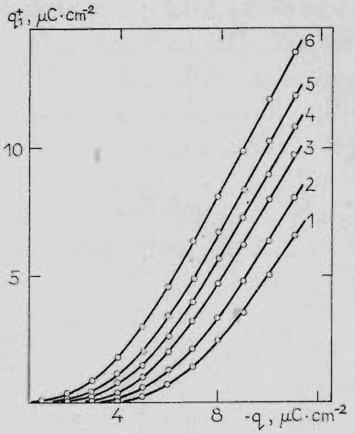

FIG. 5

The charge dependence of the amount of specifically adsorbed $N(CH_3)_4^+$ in methanol for *m*: *1* 0·05; *2* 0·1; *3* 0·2; *4* 0·3; *5* 0·5; *6* 1·0

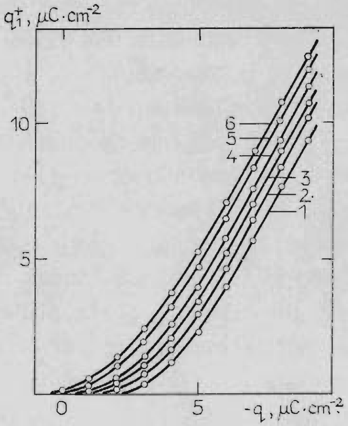

FIG. 6

The charge dependence of the amount of specifically adsorbed $N(C_2H_5)_4^+$ in ethanol for *m*: *1* 0·02; *2* 0·05; *3* 0·1; *4* 0·2; *5* 0·5; *6* 1·0

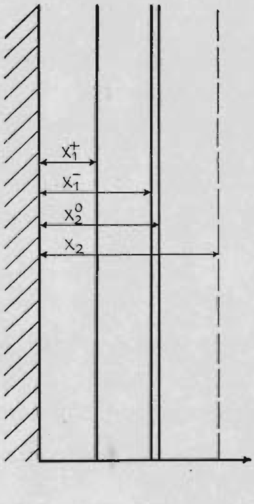

FIG. 7

The inner layer model for the adsorption of TAA ions from alcohols: x_1^+ inner Helmholtz plane for cations; x_1^- inner Helmholtz plane for anions; x_2^0 - outer Helmholtz plane in the solution of supporting electrolyte; x_2 outer Helmholtz plane in the solution of the TAA salts

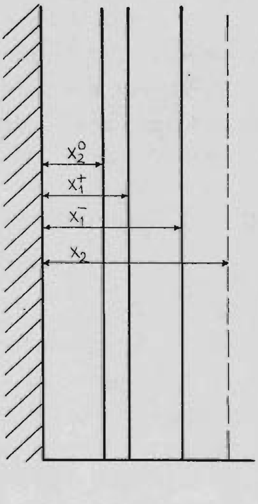

FIG. 8

The inner layer model for the adsorption of TAA ions from aqueous solutions cations. The proposed model of the inner layer in alcoholic solutions is represented in Fig. 7. According to this model the shift of the outer Helmholtz plane from the distance x_2^0 in the solution of supporting electrolyte ($q_1^+ = 0$) to the position x_2 in the solutions containing a surface-active electrolyte, is due to the entrance of the large TAA cations into the inner layer. As a result of the strong specific adsorption of the TAA cations (recharge of the electrode surface) the counter ions (ClO_4^-) enter the inner layer and localize in the plane x_1^-. Under the conditions of the ionic association in the inner layer the structure of this part of the double layer has been discussed in our previous paper for the case $x_2 = \text{const}$[10]. In the present model (Fig. 7) the distances of the planes x_2^0, x_1^+ and x_1^- from the electrode surface are considered to be independent of q_1^+. For the condition $x_2 = f(q_1^+)$ a calculation model of the inner layer parameters has been proposed in our papers[11,12].

In aqueous solutions the inner layer model is somewhat more complicated: *1*) the adsorption of organic TAA cations causes significant change in the inner layer dielectric properties. *2*) the position of the planes x_2^0 and x_1^+ can become opposite to that one in alcoholic solutions. At certain surface coverages the condition $x_1^+ > x_2^0$ can become valid (Fig. 8). Therefore the calculations based on the model in Fig. 7 yield for these conditions physically senseless results (negative inner layer capacities, improbably high repulsion between the specifically adsorbed ions *etc.*). The quantitative analysis of this model will be given elsewhere.

For $x_2 = f(q_1^+)$ the formulae for the calculation of the inner layer parameters have been derived on the basis of the model of three condensers in series[13]. According to this model the potential drop across the inner layer can be expressed by the following equation:

$$\psi^u = \psi^u_{01^+} + \psi^u_{1^+1^-} + \psi^u_{1^-2} = q/K_{01^+} + (q + q_1^+)/K_{1^+1^-} + \\ + (q + q_1^+ + q_1^-)/K_{1^-2}\,, \tag{1}$$

where the lower indexes at the potential drop ψ^u and capacity K indicate the planes between which the potential drop is located or they denote the volume with the capacity K, respectively. The quantity q_1^- is the charge of the anions in the inner layer. In the first approximation the dielectric constants of the inner layer D_{D2} can be regarded as independent of the specific adsorption of TAA cations. As the distances x_1^+ and x_1^- (Fig. 7) are considered to be constant the capacities K_{01^+} and $K_{1^+1^-}$ for $q = \text{const}$ have also constant values. In general, the dependence of K_{1^-2} on q_1^+ is unknown; however, in the first approximation the linear variation of $1/K_{1^-2}$ with q_1^+ can be suggested

$$1/K_{1^-2} = 1/K^0_{1^-2} + pq_1^+\,, \tag{2}$$

where the upper index at the capacity K means the condition $q_1^+ = 0$. Considering

Eq. (*2*), the relations[10]

$$-q_1^-/q_1^+ \cong 0{\cdot}3 \quad \text{and} \quad K^0_{1^-2} \gg K^0_{1^+2} \qquad (3)$$

and the formula for three condensers in series

$$1/K_{02} = 1/K_{01^+} + 1/K_{1^+1^-} + 1/K_{1^-2}\,, \qquad (4)$$

the Eq. (*1*) obtains the following form

$$\psi^{\mathrm{u}} \cong q/K^0_{02} + (1/K_{1^+1^-} + pq)\,q_1^+ + 0{\cdot}7(q_1^+)^2\,. \qquad (5)$$

In this stage of the derivation it is expedient to introduce the auxiliary function χ

$$\chi = (\psi^{\mathrm{u}} - q/K^0_{02})/q_1^+\,, \qquad (6)$$

the values of which can be calculated from the experimental data. The ratio q/K^0_{02} corresponds to the quantity ψ^{u} for the supporting electrolyte where $q_1^+ = 0$. It follows from Eq. (*5*) and (*6*) that

$$\chi = 1/K_{1^+1^-} + p(q + 0{\cdot}7q_1^+)\,. \qquad (7)$$

Linear experimental plots of χ against $(q + 0{\cdot}7q_1^+)$ have been obtained. It follows from this fact that p = const and, consequently, the assumption of the linear dependence of the quantities $1/K_{1^-2}$ and $1/K_{02}$ on q_1^+ is correct.

The capacity $K_{1^+1^-}$ and the term p can easily be found from Eq. (*7*). By the aid of Eqs (*3*) and (*4*) all the other inner layer capacity components (K_{02}, K_{1^+2} and K_{1^-2}) can be determined for any value of q_1^+.

On the basis of the $\chi - q_1^+$ plots the values of the terms p, K_{02}, K_{1^+2} and of the thickness ratio $(x_2 - x_1^+)/x_2$ have been determined for $q_1^+ = 0$ and for the mean specific adsorption $\bar{q}_1^+$ for the given q. The plots of K_{02}, K_{1^+2} and $(x_2 - x_1^+)/x_2$ against q are shown in Fig. 9 for the adsorption of $N(C_2H_5)_4^+$ from ethanol. It follows from Fig. 9 that for $\bar{q}_1^+ = \bar{q}_1^+$ the capacities K_{02} and K_{1^+2} are considerably lower than for $q_1^+ = 0$ and their values decrease with an increase of $-q$. The low values of the capacities K_{02} and K_{1^+2} at $\bar{q}_1^+ = \bar{q}_1^+$ witness about the significant increase of the inner layer dimensions due to the adsorption of $N(C_2H_5)_4^+$. The increase of the ratio $(x_2 - x_1^+)/x_2$ in transition from the condition $q_1^+ = 0$ to $\bar{q}_1^+$ demonstrates that the decrease of the capacities K_{02} and K_{1^+2} with the growth of q_1^+ is due to the changes in the value of x_2. The changes of the capacities at a constant value of the ratio $(x_2 - x_1^+)/x_2$ are due to the dependence of D_{02} on q_1^+.

In the table the values of the parameter p characterizing the variation of the capacity components with the charge q_1^+ are represented. As seen the values of p increase with the increase of the dimensions of the ions adsorbed specifically. This result is physically reasonable since the distance x_2 must increase the more the greater is an adsorbing ion:

Ion	$N(CH_3)_4^+$	$N(C_2H_5)_4^+$	$N(C_4H_9)_4^+$
p	$4{\cdot}4 \,.\, 10^{-4}$	$6{\cdot}2 \,.\, 10^{-3}$	$1{\cdot}0 \,.\, 10^{-2}$

The $K_{02} - q$ plots are represented in Fig. 10 for various TAA cations. It is seen that in transition from the condition $q_1^+ = 0$ to $\bar{q}_1^+$ the change of K_{02} becomes more

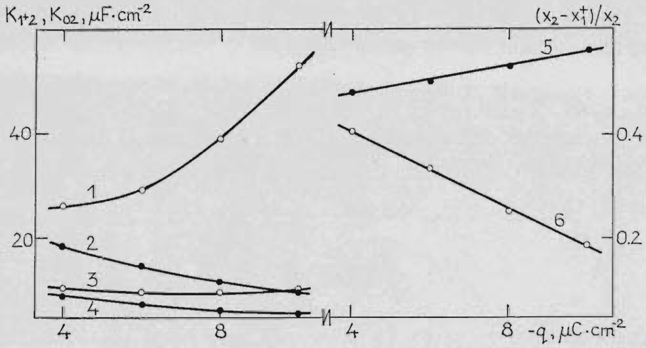

FIG. 9

Charge dependence of the inner layer parameters for the adsorption of $N(C_2H_5)_4^+$ from ethanol. *1*, *3*, *6* $q_1^+ = 0$; *2*, *4*, *5* $q_1^+ = \bar{q}_1^+$

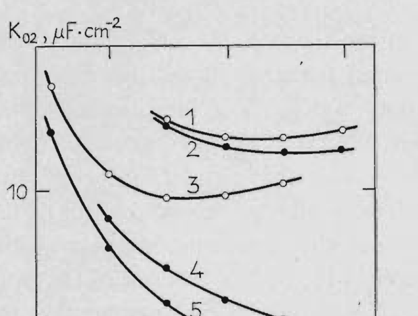

FIG. 10

Charge dependence of the integral capacity K_{02} for the adsorption of $N(CH_3)_4^+$ from methanol, $N(C_2H_5)_4^+$ and $N(C_4H_9)_4^+$ from ethanol. *1*, *3* $q_1^+ = 0$; *2*, *4*, *5* $q_1^+ = \bar{q}_1^+$

pronounced in the sequence of cations $N(CH_3)_4^+ < N(C_2H_5)_4^+ < N(C_4H_9)_4^+$, *i.e.* in the sequence of an increase of the ionic radii. Indeed, these results are physically reasonable.

Physical validity of the inner layer parameters obtained shows that the inner layer model and the calculation procedure proposed can be successfully used for the quantitative study of the specific adsorption of large ions from alcohols. Obviously, this model can be used also in other systems where the adsorption is accompanied by an increase of the inner layer dimensions but practically does not influence the inner layer dielectric properties. This model will also be valid for a quantitative description of more complicated systems, *e.g.* for the adsorption of TAA cations in aqueous solutions.

An increase of the distance x_2 and a decrease of the inner layer capacity due to the specific adsorption of TAA cations (Fig. 9 and 10) must also be reflected in the shape of the differential capacity curves of the electrode. As seen in Figs 1 and 2, this effect causes the braking of the capacity increase with the growth of the negative potential of the electrode. In the case of the large TAA cations the differential capacity begins to increase at sufficiently high negative potentials.

On the basis of the results obtained the following conclusion can be made. So far as the TAA cations have the properties both of molecules and ions, the adsorption behaviour of the TAA cations has a dualistic nature in aqueous solutions; in contrary, in alcoholic solutions their adsorption can be regarded as of typical ions with large dimensions. Therefore, in the double layer studies on ideally polarizable electrodes the variation of the solvent nature allows to extend considerably the number of problems the solution of which is almost impossible on the basis of a single solvent (for example, water).

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