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INVESTIGATION OF THE ADSORPTION OF TETRAALKYLAMMONIUM SALTS AT THE NITROBENZENE/WATER INTERFACE

L. I. Boguslavskii, A. N. Frumkin,
and M. I. Gugeshashvili

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The present work is devoted to an elucidation of the structure of the electric double layer at the nitrobenzene/water interface in the presence of tetraalkylammonium halides. A model is proposed, according to which the adsorbed cation and anion are in different phases on different sides of the interface. The conclusions drawn from a comparison of the data on the variation of the distribution potentials with changing free energy of adsorption confirm the applicability of the proposed model.

The present work is devoted to a study of the adsorption of tetraalkylammonium salts at the nitrobenzene/water interface under equilibrium conditions.

The adsorption was found according to the change in the interfacial tension, measured by the method of determination of the weight and volume of the drop, which is broken off from the end of the capillary tube under the action of the force of gravity [1]. The surface tension σ was determined according to the formula

$$\sigma = \frac{v(d_1-d_2)F_g}{r}, \qquad (1)$$

where d_1 and d_2 are the densities of the investigated liquids; v is the volume of the drop; g is the acceleration of the force of gravity; F_g is a correction function, which was found according to the Harkins–Brown table [2]; r is the radius of the capillary.

For measurements of σ we used an instrument consisting of a glass capillary, a syringe with a 1 cm^3 capacity, a micrometer, and a vessel for the test liquid. The inner diameter of the capillary was equal to 0.6-0.8 mm, which ensured sufficiently accurate measurement of the tension in the interval 1-50 dyn/cm. The lifetime of the drop was no less than 2 min, which was necessary to establish adsorption equilibrium [2, 3].

Figure 1 presents the dependence of the interfacial tension on the logarithm of the concentration of tetraalkylammonium halides [4]. The largest concentration corresponds to the maximum solubility. In the series chlorides–bromides–iodides, the solubility in water decreases [6]. The initial concentration of the salt in aqueous solution $c = c_n + c_w$. Knowing the distribution coefficient $S = c_n/c_w$, we can determine the true concentration of the tetraalkylammonium salt in the aqueous phase of the equilibrium system nitrobenzene/water (the volumes of the aqueous and nonaqueous phases are the same):

$$c_w = \frac{c}{1+S} \qquad (2)$$

If $S \ll 1$, c_w can be considered equal to c with a sufficient degree of accuracy.

The distribution coefficients S of tetraalkylammonium salts in the nitrobenzene–water system were taken from [5].

From the data on the interfacial tension, using the Gibbs adsorption equation

$$\Gamma = -\frac{1}{2RT}\frac{d\sigma}{d\ln c} \qquad (3)$$

we constructed the adsorption isotherms for tetraalkylammonium chlorides, bromides, and iodides (Fig. 2a, b, c). Figure 3a, b, presents these isotherms in reduced coordinates $\theta = f(y)$, where θ Γ/Γ_∞, $y = c/c_{\theta=0.5}$ [3].

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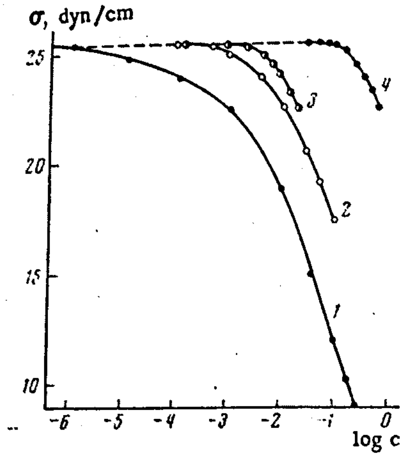


Fig. 1

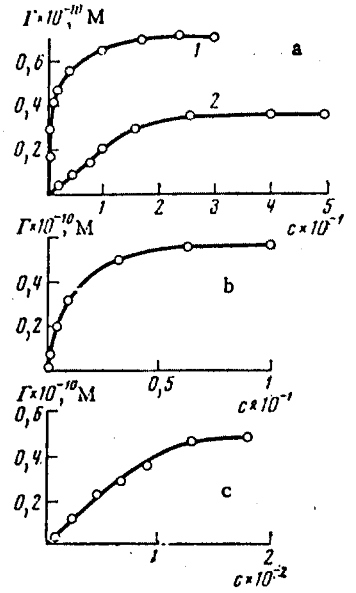


Fig. 2

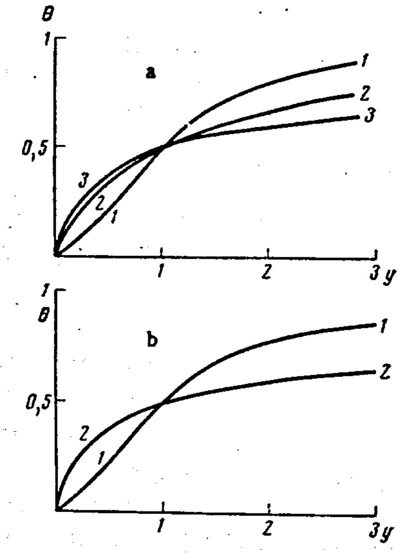


Fig. 3

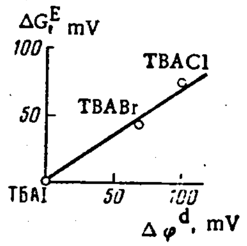


Fig. 4

Fig. 1. Dependence of the interfacial tension σ on the concentration of tetraalkylammonium salts: 1) TBACl; 2) TBABr; 3) TBAI; 4) TEACl.

Fig. 2. Isotherms of the adsorption of tetraalkylammonium salts. a: 1) TBACl, 2) TEACl; b) TBABr; c) TBAI.

Fig. 3. Isotherms of the adsorption of tetraalkylammonium salts in reduced coordinates. a: 1) TBAI, 2) TBABr, 3) TBACl; b) TEACl; 2) TBACl.

Fig. 4. Dependence of the difference of the free energy of adsorption $\Delta\varphi^d$ [5], calculated relative to the data for TBAI.

TABLE 1

Salt	According to the slope of the initial portion		According to the Frumkin isotherm	
	B	$\lg B$	B^F	$\lg B^F$
TBAI	$6{,}3 \cdot 10$	1,82	$5{,}7 \cdot 10$	1,75
TBABr	$3{,}6 \cdot 10^2$	2,5	$3{,}6 \cdot 10^2$	2,5
TBAB + KBr	$7 \cdot 10^2$	2,85	$8 \cdot 10^2$	2,9
TBACl	$7 \cdot 10^2$	2,85	$8 \cdot 10^2$	2,9
TBACl + KCl	$1{,}9 \cdot 10^3$	3,28	$1{,}94 \cdot 10^3$	3,29
TEACl	4,5	0,65	4,5	0,65

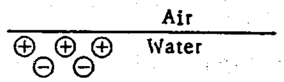
As can be seen from Fig. 2a, b, c, the dependence $\Gamma = f(c)$ approaches saturation. The value of Γ at the most accessible concentration of the salt is taken as Γ_∞.

With increasing radius of the anion from Cl^- to I^-, the contact interaction between adsorbed particles increases, which agrees with the data known from the literature for the water/air interface (Fig. 3, a). On the contrary, with increasing radius of the cation from TEA^+ to TBA^+, the contact interaction decreases at the nitrobenzene/water interface (Fig. 3b). The pattern observed in this case for cations (Fig. 3, b) is opposite to that known from the literature [4] for the water/air interface.

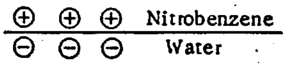
The presence of a supporting electrolyte (Table 1) increases the value of the adsorption equilibrium constant B, which is shown for the example of tetrabutylammonium chloride and bromide, investigated in the presence of 10^{-2} M KCl and 10^{-2} M KBr, respectively. The constant B was found according to the initial slope of the adsorption isotherm, and also calculated according to the Frumkin isotherm.

The nonobservance of the Traube rule indicates that the treatment of the results used for the interface of water with air and mercury [4] is inapplicable in this case. The main difference lies in the fact that evidently the tetraalkylammonium cation is capable of a greater or lesser degree of penetration into the nitrobenzene phase, depending on the radius. In this case the basic conditions ensuring fulfillment of the Traube rule – additivity of the work required for the repulsion of each link of the hydrocarbon chain from the aqueous phase – is not fulfilled, since the ion is able to be partially transferred to the nitrobenzene phase. If the adsorbed cations were only in the aqueous phase, then the attractive interaction between them would increase with increasing size of the cation. If, however, we assume that the cation can pass through the interface, then the picture of the structure of the electrical double layer should be different.

In the adsorption of TEA^+, its penetration into nitrobenzene is minor,* and the structure of the interface is identical with that existing at the water/air interface:



If, however, TBACl is dissolved in the system, then the TBA^+ cation is redistributed between water and nitrobenzene in such a way that the structure of the interface can be schematically represented in the form:



Now the cation and anion are on different sides of the interface, and the dipoles, oriented uniformly, exhibit a repulsive interaction, which is evident from the adsorption isotherm of this salt in the nitrobenzene-water system (Fig. 3).

In the presence of an indifferent electrolyte, there is a change in the parameters of the adsorption isotherm (Table 1). The value of B increases, which is an indication of an increase in the hypothetical work on the transport of the adsorbed particle from the volume of the aqueous solution into nitrobenzene at the interface. An increase in the ionic strength of the solution leads to an increase in the surface activity of the salt (TBACl, TBABr).

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*On the basis of the data obtained according to the equilibrium distribution of tetraalkylammonium halides, in the nitrobenzene–water system the tetraethyllammonium cation penetrates into nitrobenzene 10^4 times worse than the tetraalkylammonium cation.

According to Table 1, the constant of the adsorption equilibrium B^F, found according to the initial slope of the adsorption isotherm (or according to the Frumkin adsorption equation) increases with increasing radius of the anion. The change in the values of the adsorption equilibrium constants B^F of the two salts compared can be expressed in electrical units and compared with the change in the distribution potential φ^d of these salts (Fig. 4).

The change in B^F, plotted along the vertical axis of Fig. 4 and expressed in electrical units, takes the form

$$\Delta\varphi^{F}_{(\text{TBAX}-\text{TBAI})} = \frac{RT}{F}\ln\frac{B^{F}_{\text{TBAX}}}{B^{F}_{\text{TBAI}}}, \tag{4}$$

where X = Cl^-, Br^-.

As can be seen from the figure, there is a direct relationship between $\Delta\varphi^d$ and $\Delta\varphi^F$ when the nature of the anion changes. In order to reveal the meaning of this correlation, we should consider that the quantity B^F characterizes the free energy change when a particle is transferred from the volume of the solution to the surface layer. In other words, the value of B^F can be considered proportional to the distribution coefficient of the ion between the solution and the surface layer S' in which adsorption occurs.

Making this assumption, we find that

$$\Delta\varphi^{F}_{(\text{TBAX}-\text{TBAI})} = \frac{RT}{F}\ln\frac{S'_{\text{TBAX}}}{S'_{\text{TBAI}}}. \tag{5}$$

The latter expression can be compared with expression (6) for the change in the distribution potentials of the salts TBAX and TBAI between water and nitrobenzene:

$$\Delta\varphi^{d}_{(\text{TBAX}-\text{TBAI})} = \frac{RT}{F}\ln\frac{S_{\text{TBAI}}}{S_{\text{TBAX}}}. \tag{6}$$

According to the results presented in Fig. 4, $\Delta\varphi F \approx \Delta\varphi^d$. Therefore, setting (5) and (6) equal, we find that there is an inverse proportionality between the values of S and S':

$$\frac{S_{\text{TBAI}}}{S_{\text{TBAX}}} = \frac{S'_{\text{TBAX}}}{S'_{\text{TBAI}}}. \tag{7}$$

With a common cation, the salt that has a larger distribution coefficient S is not adsorbed as well – it has a lower distribution coefficient between the aqueous phase and the surface layer S'. In the case under consideration, the coefficient of correlation between water and nitrobenzene increases in the sequence from tetrabutylammonium chloride to the iodide; the quantity S', on the other hand, proportional to the adsorbability, drops when considered in the same sequence.

This unexpected result can be tentatively explained on the basis of a model according to which the adsorbed cation and anion are in different phases on opposite sides of the interface. In this case, the energy of their interaction will increase with decreasing distance between them. Therefore, the adsorption of an anion with a smaller radius should be energetically more profitable than the adsorption of an anion with a larger radius, if we take into consideration only the crystallographic radii, i.e., consider that the hydrate shell of the anion does not prevent its approach to the cation.

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