of the absorbing layer for the KLT/copper and KLT/glass systems indicates a monoenergetic character of the radiation. In contract, inhomogeneous radiation is observed for the KLT/aluminum system. These results apparently can be explained by a significant contribution of the characteristic radiation of the substrate material, appearing at such high values of accelerating voltage V.

In this connection we should note that, owing to the limitations of the method used for determining photon energy, it is not possible to identify the spectra obtained, and the numerical values that have been cited are quite approximate. However, the results do suggest that the photon emission observed when an adhesive contact is broken is the result of retardation of high-energy electrons in the substrate material, and that this emission is x-ray radiation.

The results obtained in the present work also show that the energy of the electrons in breakdown of an adhesive contact are on the order of tens of keV; this same level of energies has been indicated in previous studies using different methods [6].

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ADSORPTION AND BOUNDARY POTENTIALS IN WATER—NITROBENZENE AND WATER—OCTANE SYSTEMS IN THE PRESENCE OF TETRAALKYLAMMONIUM HALIDES

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The purpose of the present work was to investigate the properties of the water—nonaqueous-phase interface in a braod range of simple and thoroughly studied objects and specifically in the homologous series of C_3-C_7 tetraalkylammonium halides.† Nitrobenzene (D = 36.1) and octane (D = 2) were selected as the nonaqueous phases. The nitrobenzene used in the experiments was graded "for Kerr cells," and the octane was "kh.ch." ["chemically pure"] grade. The methods used to prepare the solutions and the purity of the tetraalkylammonium salts used have been described in [1].

*Deceased.

†The chlorides and bromides of tetrapropylammonium $N(Pr)_4^+$, tetrabutylammonium $N(But)_4^+$, tetrapentylammonium $N(Pe)_4^+$, tetrahexylammonium $N(Hex)_4^+$, and tetraheptylammonium $N(Hept)_4^+$.

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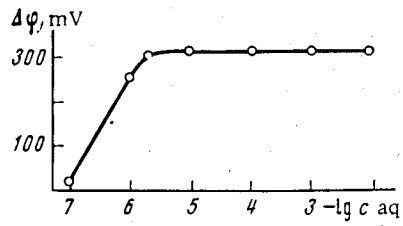

Fig. 1

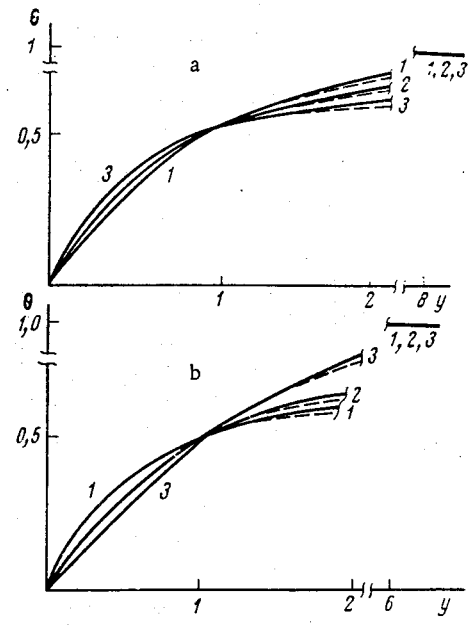

Fig. 2

Fig. 1. Dependence of the changes in the Volta effects measured in a water–nitrobenzene system in cell (1) on the concentration of $N(Pe)_4Cl$ in the water.

Fig. 2. Sorption isotherms of tetraalkylammonium chlorides in water–nitrobenzene (a) and water–octane (b) systems in reduced coordinates: 1) $N(Pr)_4^+$; 2) $N(Pe)_4^+$; 3) $N(Hept)_4^+$. The dashed lines are the theoretical isotherms calculated from Frumkin's equation.

The changes in the potential jump on the water–nitrobenzene or water–octane interface under investigation were measured by the vibrating-electrode method [2] in the following cell:

$$\text{Au} \;\big|\; \text{air} \;\big|\; \begin{matrix}\text{nonaqueous}\\ \text{phase}\end{matrix} \;\big|\; \begin{matrix}\text{water}\\ (\text{Alk})_4\text{NX}\end{matrix} \;\big|\; \begin{matrix}\text{saturated aqueous}\\ \text{KCl solution}\end{matrix} \;\big|\; Hg_2Cl_2, Hg \qquad (1)$$

The measured potentials have positive values and depend on the concentration of the tetraalkylammonium salt. As the concentration is increased, these potentials increase, and at high concentrations they reach limiting values (Fig. 1). As a comparison shows, in the water–nitrobenzene system the differences between the limiting potentials corresponding to two salts with a common ion coincide with the potentials calculated from the distribution coefficients according to the equation

$$\Delta\varphi = \varphi_{M_1X} - \varphi_{M_2X} = \frac{RT}{F}\ln\frac{S_{M_1X}}{S_{M_2X}} = \frac{RT}{2F}\ln\frac{S_{M_1}}{S_{M_2}}, \qquad (2)$$

where the S_{MX} are the distribution coefficients of the salts (the indices M_1X and M_2X refer to two salts with a common anion), and the S_M are the distribution coefficients of the cations. The distrubution coefficients of the tetraalkylammonium salts were determined from measurements of the conductivities of the aqueous and nitrobenzene fractions of the water–nitrobenzene system [1]. Table 1 presents the values of limiting potentials, which were measured in cell (1) and calculated from Eq. (2) on the basis of experimental data for potassium iodide ($1/S = 5.5 \cdot 10^3$) [3].

The condition that the difference between the limiting potentials of two salts is independent of the nature of the common ion, which is consistent with Eq. (2) and the thermodynamic theory of distribution potentials [4], is fulfilled for all the tetraalkylammonium salts investigated. However, the potentials measured in the region of low concentrations do not follow Eq. (2) (Fig. 1) [5].

The adsorption was measured from the changes in the surface tension of the aqueous solutions of the tetraalkylammonium salts on the boundaries with nitrobenzene and octane ac-

TABLE 1. Comparison of the Limiting Potentials Measured in Cell (1) with the Potentials Calculated from the Conductivities of the Solutions by means of Eq. (2)

Cation	Cl⁻		Br⁻	
	$\Delta\varphi_{mea}$, mV	$\Delta\varphi_{calc}$, mV	$\Delta\varphi_{mea}$, mV	$\Delta\varphi_{calc}$, mV
$N(Pr)_4^+$	140	137	110	117
$N(But)_4^+$	165 [9]	158 [9]	130	130
$N(Pe)_4^+$	255	252	230	130
$N(Hex)_4^+$	280	283	252	249
$N(Hept)_4^+$	310	304	280	269

cording to the method described in [8]. The results obtained from the changes in the surface tension in the water–octane system are consistent with the data in the literature [7, 8].

Gibbs' adsorption equation was used to calculate the adsorption and to construct the sorption isotherms of the salts investigated, which are presented in Fig. 2 in reduced coordinates for the tetraalkylammonium chlorides. The calculation was carried out under the assumption that the salts are completely dissociated in the aqueous phase and with the replacement of the activities by concentrations. The isotherms were obtained in the concentration range where $\Delta\Phi$ remains unchanged, and they can be described formally by Frumkin's equation [9]. In the water–nitrobenzene system the salt with the largest cationic radius $N(Hept)_4Cl$ has the most arched isotherm. As the radius of the cation is decreased, the sorption isotherms become less arched and become almost S-shaped in the case of $N(Pr)_4Cl$ (Fig. 2a, curve 1). The law obtained for the changes in the shape of the isotherm as a function of the radius of the adsorbed particle is contrary to the law known from the literature for the water–air and water–mercury interfaces [10]. This allowed us to propose a model of the structure of the electric double layer, in which the oleophilic cations are located in the nitrobenzene, while the anions are located in the water. A repulsive interaction which increases with the size of the cation should appear in a double layer designed in this manner.

In the water–octane system the salt with the smallest cation $N(Pr)_4^+$ has the most arched isotherm (Fig. 2b), and the salt with the largest cation $N(Hept)_4^+$ has the most nearly S-shaped isotherm. Such a law for the changes in the shape of the isotherm in the water–octane system is the opposite of that observed in the water–nitrobenzene system, and this suggests that in this case the double layer is concentrated mainly in the water. Table 2 presents the empirical values of the limiting adsorption Γ_∞, values of the attraction constant a, as well as the fraction of the area A which is covered by the adsorbed particles in the case of the limiting adsorption as functions of the radius of the cation in the tetraalkylammonium salt. The value of A was calculated from the relation

$$A = \pi r^2 N \Gamma_\infty, \tag{3}$$

where r is the radius of the cation, and N is Avogadro's number.

As we see from the data in Table 2, at the empirical values of the limiting adsorption corresponding to the saturation region on the $\Gamma = \Gamma(c)$ curve, the water–nitrobenzene interface is only partially covered. This type of filling may be attributed to a repulsive interaction between the particles adsorbed on the interface. On the other hand, the calculation of the values of a in the water–octane system revealed that a increases with increasing radius of the cation (Table 2). This suggests that there is an increase in the attraction between the adsorbed particles. This is graphically demonstrated by the calculation of the fraction of the area A closed off by the adsorbed particles on the water–octane interface.

From the data in Table 2 it is also seen that the cations with the small radius $[N(Pr)_4^+]$ occupy less than half of the water–octane surface, while the cations with the large radius $[N(Hept)_4^+]$ can find room on the surface, only if we assume that the centers of the cations are not located in one plane.

TABLE 2. Values of the Parameters of the Adsorption Layer for the Tetraalkylammonium Chlorides and Bromides in the Water–Nitrobenzene and Water–Octane Systems as Functions of the Radius of the Cation (Å)

Parameter	$N(P_2)_4^+$, $r=3,8$	$N(Pe)_4^+$, $r=5,2$	$N(Hex)_4^+$, $r=6,0$	$N(Hept)_4^+$, $r=6,8$
Water – nitrobenzene (chlorides)				
a	0	−0,4	−0,7	−1,2
$\Gamma_\infty \cdot 10^{10} \pm 0,1$	0,7	0,5	0,5	0,4
A	0,18	0,25	0,31	0,35
Water – octane*				
a	0 / −0,7	0,2 / −0,5	0,3 / −0,2	0,7 / 0,6
$\Gamma_\infty \cdot 10^{10} \pm 0,1$	1,0 / 1,6	1,0 / 1,7	1,3 / 1,8	1,8 / 1,9
A	0,3 / 0,4	0,5 / 0,9	0,9 / 1,2	1,6 / 1,7

*The values above the lines are for the chlorides, and those below the line are for the bromides.

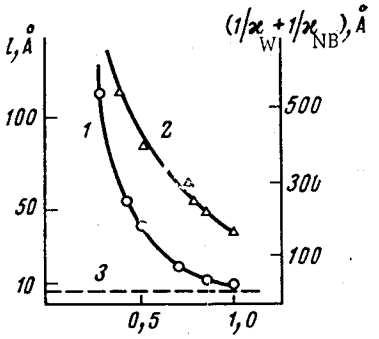

Fig. 3. Dependence of the effective thickness of the electric double layer (1) and the sum of the Debye lengths in water and in nitrobenzene (2) on the degree of filling of the interface in the system containing $N(Pe)_4Cl$. Sum of the crystallographic radii of the cation and anion (3).

The value of the coefficient in Traube's rule in the water–octane system, which is calculated as $\sqrt{c_n/c_{n+1}}$ is equal to $\sqrt[3]{10} \cong 2.2$. The concentrations c_n and c_{n+1} of two members of the homologous series of tetraalkylammonium salts cause the same effect with respect to changes in the Volta effect ($\Delta\varphi = 40$ mV) or σ ($\Delta\sigma = 2$ dyne/cm). This value of the coefficient is consistent with the data in [10, 12], in which similar values of the coefficient in Traube's rule were presented for the water–air and water–mercury interfaces.

In order to obtain a more definite picture of the structure of the electric double layer on the water–nonaqueous-phase interface, we calculated the effective thickness of an assumed dense electric double layer (l) and the sum of the Debye lengths in water and nitrobenzene ($1/\kappa_W + 1/\kappa_{NB}$). The effective thickness of the double layer is $l = \mu D/\bar{e}$ (where $\bar{e}$ is the elementary charge, and μ is the dipole moment of the adsorption layer). The dielectric constant D in the region of the double layer in the water and the nitrobenzene was assumed to be 30. The value of μ was calculated from the Helmholtz equation

$$\Delta\varphi = 4\pi n \mu \theta,$$

where $\Delta\varphi$ is the change in the interphase potential jump, n is the number of particles per square centimeter of surface with maximum filling, which was determined from Γ_∞, and θ is the degree of filling of the surface. The Debye lengths in water and nitrobenzene were calculated from the relation

$$\varkappa = \left(\frac{4\pi F^2}{DRT} c_i\right)^{1/2},$$

where c_i is expressed in moles per cubic centimeter, and F is Faraday's number. Figure 3 presents the data for the water–nitrobenzene system $N(Pe)_4Cl$. Curve 1 is a plot of the variation in the value of ζ as a function of the degree of filling of the interface in a system with nitrobenzene. The variation in the sum of the Debye lengths in water and nitrobenzene is shown by curve 2. The sum of the crystallographic radii of the cation and anion is denoted by dashed line 3. At small values of θ curves 1 and 2 are close to one another; however, as we approach $\theta = 1$, curve 2 asymptotically approaches line 3. This indicates that the electric double layer, which is diffuse at low degrees of filling, becomes dense at high degrees of filling.

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