DISTRIBUTION POTENTIALS OF TETRAALKYLAMMONIUM HALIDE SALTS IN A SYSTEM OF WATER AND NITROBENZENE OF VARIOUS DEGREES OF PURITY

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A study of the water–nitrobenzene system in the presence of a homologous series (from C_1 to C_7) of tetraalkylammonium halide salts showed that at sufficiently high concentration of the tetraalkylammonium salts, the distribution potentials of these salts are established according to the thermodynamic theory of distribution potentials [1, 2]. However, counter to the thermodynamic theory, in the region of low salt concentrations, a concentration dependence is observed for the potential jump. A hypothesis [3] was put forward to explain this discrepancy, according to which the effect of impurity ions becomes significant with decreasing concentrations and thus the potentials measured are not the distribution potentials of the tetraalkylammonium salts.

In all previous works, we used "for Kerr cells" grade nitrobenzene without further purification. The solutions of the tetraalkylammonium salts were prepared in double-distilled water by a procedure described in our earlier work [2]. Most of the salts were twice recrystallized. The chlorides and bromides of $TPeA^+$, $THexA^+$ and $THeptA^+$* from the Lawson and Serva companies were not subjected to purification.

It was of interest to repeat the experiments, retaining the previous conditions, but using more pure nitrobenzene as this would allow evaluation of the effect of the impurities found in the nitrobenzene samples.

Unfortunately, we did not have available a sample of nitrobenzene with control parameters close to those of the samples used in our previous work [4] (Table 1). A sample of "for Kerr cells" trade nitrobenzene was prepared at our request by the Cherkassk Chemical Reagents Factory and subjected to further purification by an industrial method (Table 1). For comparison, parameters of nitrobenzene samples used in our earlier work [1, 2] are presented in Table 1.

TABLE 1. Indices Corresponding to Nitrobenzene of Various Degrees of Purity

Nitrobenzene	Solvent parameters				
	liquid appearance	crystallization temperature, °C	index of refraction n_D^{20}	density at 20°C, g/cm³	specific resistance, Ω · cm
Maximum degree of the system [4]	Colorless	5,76	1,5526	1,20324	Not less than $0{,}3 \cdot 10^8$
"For Kerr cells" grade:					
purified by the industrial method	Light yellow	5,3–5,4	1.5516	1,2	10^8
used in earlier works [1, 2]	Yellow	5,2	1,5512	1,2	$0{,}3 \cdot 10^8$

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* Hereinafter $TPeA^+$ represents tetrapentylammonium, $THexA^+$ represents tetrahexylammonium and $THeptA^+$ represents tetraheptylammonium.

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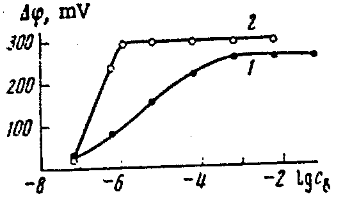

Fig. 1. Dependence of the change in the Volta potentials measured in circuit (1) on the concentration of TPeACl in water: 1) in the system with unpurified nitrobenzene and 2) in the system with nitrobenzene purified by the industrial method (see Table 1).

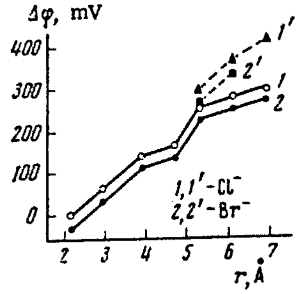

Fig. 2

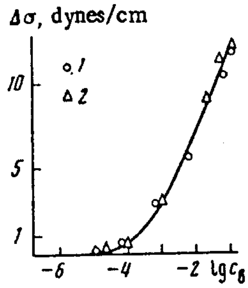

Fig. 3

Fig. 2. Dependence of the limiting potentials measured in circuit (1) on the dimension of the cation: 1 and 2) system with unpurified nitrobenzene and 1' and 2') system with purified nitrobenzene.

Fig. 3. Dependence of the interphase tension on the concentration of TPeACl in water for the system with purified (1) and unpurified (2) nitrobenzene.

The change in the potential jump at the water–nitrobenzene phase boundary was measured by the dynamic capacitor method [5] in the circuit

$$\mathrm{Au}\;\Big|\;\mathrm{Air}\;\Big|\;\mathrm{Nitrobenzene}\;\Big|\;\begin{matrix}\mathrm{Water}\\ \mathrm{(Alk)_4NX}\end{matrix}\;\Big|\;\begin{matrix}\mathrm{KCl}\\ \mathrm{sat.}\end{matrix}\;\Big|\;\begin{matrix}\mathrm{Hg_2Cl_2}\\ \mathrm{Hg}\end{matrix}\;. \qquad (1)$$

Figure 1 shows the dependence of the change in the value of the Volta potential measured in circuit (1) on the concentration of TPeACl in water. As seen from the figure, both dependences have the form of curves reaching saturation. In the system with unpurified nitrobenzene (curve 1), the limiting value of the Volta potential corresponding to the distribution potential of TPeACl [2] is established starting at a concentration of about $6.3 \cdot 10^{-4}$ M and is equal to 260 mV. However, in the system with purified nitrobenzene (curve 2), the limiting value of the Volta potential is already reached at a concentration of about 10^{-6} M and is equal to 290 mV. It is striking that in the system with purified nitrobenzene, the limiting value of the potential is reached sharply in a jump: 10^{-6} TPeACl concentration corresponds to the potential jump at 290 mV. However, in the system with unpurified nitrobenzene, the change in the potential is only 100 mV.

The change in the Volta potential in circuit (1) containing purified nitrobenzene in the presence of $\mathrm{THexA^+}$ and $\mathrm{THeptA^+}$ chlorides and $\mathrm{TPeA^+}$ and $\mathrm{THexA^+}$ bromides showed that in this case the values for the limiting potentials are higher than in the system with unpurified nitrobenzene. This is seen from Fig. 2 in which the dependence of the limiting Volta potentials measured in circuit (1) on the size of the cation are given.

The distribution potentials of two salts MX with a common ion, for example, with a common anion, are related by the formula

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

where the indices M_1X and M_2X relate to the two salts with a common anion.

As shown by calculation according to Eq. (2), the difference in the limiting potential measured in circuit (1) (curves 1' and 2') are independent of the nature of the common ion and the salt concentration, that is, the difference is the distribution potential of the TPeACl, TPeABr, THexACl, THexABr, and THeptACl salts in the system with purified nitrobenzene.

The measurement of the interphase tension at the phase boundary of the aqueous TPeACl solutions/nitrobenzene according to the drop weight determination method [6] showed that the purification of nitrobenzene has no effect, within the limits of experimental precision, on the interphase tension. This is seen from Fig. 3 in the dependence of the interphase tension in the nitrobenzene–water system on the TPeACl concentration in water. It is seen that the measurements in systems containing purified and unpurified nitrobenzene give coincident results.

Thus, it was possible to show in the present work that the presence of impurities in nitrobenzene affects the value of the distribution potential of tetraalkylammonium salts as even the incomplete purification of the sample of nitrobenzene used in the present work significantly broadens the range of concentrations in which the thermodynamic theory of distribution potentials is applicable.

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INFLUENCE OF THE CONCENTRATION OF SODIUM SULFIDE IN ALKALI ON THE ANODIC ACTIVITY OF A SMOOTH IRON ELECTRODE

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In the study of an iron powder electrode it was established that the dependence of its discharge capacity on the concentration of Na_2S in an alkaline electrolyte is extremal in character (Fig. 1, curves 1 and 2) [1]. In the case of sintered electrodes, the dependence is given by a curve with a maximum corresponding to 10^{-1} N Na_2S. For nonsintered electrodes at the same sulfide concentration, a minimum is observed, due to deterioration in the contact properties of the mass as a consequence of the accumulation of nonconducting iron hydroxide. The aim of the present work was to study the influence of the concentration of Na_2S in aqueous KOH solution on the anodic activity of a smooth iron electrode.

The determination of the discharge capacity of the electrodes and the identification of the electrochemical processes were carried out by a potentiodynamic method using the procedure described in [2]. The rate of change in the potential was 0.25 V/h, and the rate of movement of the chart was 60 mm/h. The products of the anodic oxidation of iron were studied by x-ray diffraction using a URS-50I apparatus with $FeK_{\alpha\beta}$ radiation. A 5 N solution of cp grade KOH was used as electrolyte. Na_2S was added in the form of analytically pure grade $Na_2S \cdot 9H_2O$. The experiments were carried out on electrodes of two types. The first consisted of a polished cylinder [2] of ZhS–O iron with a surface area of 6 cm^2, which after preliminary cathodic polarization for a period of 1 h at $\varphi = -1.4$ V in pure KOH was transferred rapidly to the electrolyte with the given Na_2S

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