

The presence of a slow adsorption step in above solutions is confirmed by the plots of the resistive and reactive component of faradaic impedance against $1/\sqrt{\omega}$ (Fig. 2). An intersection of these impedance components at high frequencies is characteristic for the presence of an adsorption process in the overall electrode process [2]. Similar dependences of R_S and X_S on $1/\sqrt{\omega}$ were found in all other solutions, with the exception of oxygen-saturated 0.25 and 0.50 N KCl solutions.

In oxygen-saturated 0.25 and 0.50 N solutions, the dependence of $\text{ctg } \theta$ on $\sqrt{\omega}$ is different from that found in the first case (Fig. 3). The literature does not contain any analysis of such $\text{ctg } \theta - \sqrt{\omega}$ dependence. However, this dependence points to the absence of adsorption. We conclude from the plots of R_S and X_S against $1/\sqrt{\omega}$ (Fig. 4), according to [3], that charge transfer, a homogeneous chemical reaction, and diffusion of the reacting species are the slow steps. The charge transfer resistance appears to be caused by the difficulty of metal ionization when a salt film is present on the surface. Slow diffusion can be caused by the migration of the Tl(I) ions across the salt film to the layer next to the electrode. Low Tl(I) concentration in the layer next to the electrode also appears to delay thallium chloride formation.

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INFLUENCE OF THE METAL ON ELECTRIC DOUBLE-LAYER STRUCTURE IN DIMETHYL SULFOXIDE II. COMPARISON OF ELECTRIC DOUBLE-LAYER STRUCTURE ON Hg AND EUTECTIC In-Ga ALLOY IN SOLUTIONS OF HALIDE ANIONS AND ALKALI-METAL CATIONS

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UDC 541.135.52

It has been shown in the preceding communication [1] that the specific interaction of eutectic In-Ga alloy with the solvent is increasing as one goes from water to dimethyl sulfoxide (DMSO), and that this effect is larger than it is in the case of the mercury electrode. It was of interest to compare electric double-layer structure on Hg and on In-Ga alloy in water and in DMSO with solutions of surface-active anions. To this end we measured the potential dependence of differential capacity in 0.1 N NaClO_4 , NaBr, and NaI in water and in DMSO at a dropping electrode of eutectic In-Ga alloy using an ac bridge.† The ClO_4^- ion exhibits surface activity at In-Ga alloy, neither in water [2] nor in DMSO [1]. Reference electrode was a saturated calomel electrode (sce) in water. The DMSO purification and the method and conditions of the measurements were the same as in [1]. The capacity measured did not depend on ac frequency, and corresponded to the electric

* Deceased.

† Measurements in chloride solutions were not made, owing to the low solubility in DMSO.

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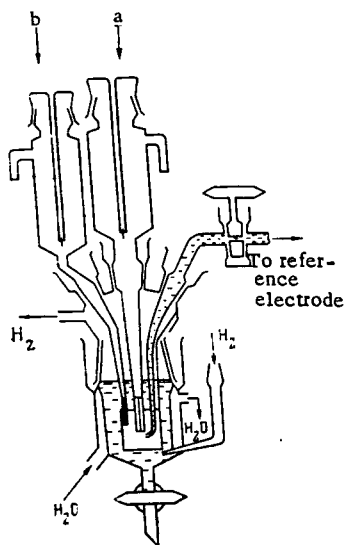


Fig. 1

Fig. 1. The cell for measuring in the same solution the differential capacity at the dropping electrode and the potential of zero charge at the streaming electrode: a) the dropping electrode, b) the streaming electrode.

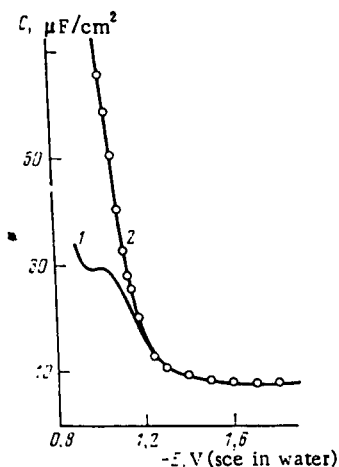


Fig. 2

Fig. 2. The C-E curves at In-Ga alloy in 0.1 N solutions: 1) NaClO₄, 2) NaBr (solid line) and NaI (points).

TABLE 1. Values for $\Delta E_{Q=0}$ and $C_{Q=0}$ at Hg and at In-Ga Alloy in DMSO Solutions of Bromides and Iodides

Solvent	Electrode of eutectic In-Ga alloy				Hg electrode	
	$\Delta E_{Q=0}, V$		$C_{Q=0}, \mu F/cm^2$		$\Delta E_{Q=0}, V$	
	Br ⁻	I ⁻	Br ⁻	I ⁻	Br ⁻	I ⁻
DMSO	0.07	0.07	70	70	0.17	0.27
H ₂ O	0.06	0.14	57	71	0.10	0.26
AN	-	-0.44	-	70	-	-

double-layer capacity. The potential of zero charge, $E_{Q=0}$, of the In-Ga alloy in the solutions studied was found, both by back-integration of the C-E curves and with the aid of a streaming electrode (Fig. 1) [1]. Data on electric double-layer structure at the mercury electrode in aqueous solutions were taken from [3], those in DMSO from [4].

The experimental values for the negative zero-charge potential shifts $\Delta E_{Q=0}$, and for the differential capacity at zero charge, $C_{Q=0}$, at Hg and at In-Ga alloy in 0.1 N NaBr and NaI in DMSO, in water, and in acetonitrile (AN) are compiled in Table 1. The quantity $\Delta E_{Q=0}$ was used by us as a measure of the surface activity of the anions in the different solvents. This is only permissible when the values of electrode capacity with the same electrolyte in different solvents at the zero-charge potential are substantially the same (cf. Table 1). The data for AN are of interest since the specific interaction of In-Ga alloy with AN is weaker than with water molecules [5].

The potential dependence of differential capacity at In-Ga alloy in 0.1 N NaClO₄, NaBr, and NaI in DMSO is reported in Fig. 2.

It can be seen from Table 1 that the influence of the solvent on the size of $\Delta E_{Q=0}$ in solutions of a given anion depends on the metal. The $\Delta E_{Q=0}$ values increase at Hg when water is replaced by DMSO, which indicates that the adsorbability of the halide anions increases as one goes from water to DMSO.

The solvation energy of the anions is known to decrease with increasing anionic radius in protic solvents, but to increase in dipolar aprotic solvents. Therefore the influence of the solvation energy of the anions on

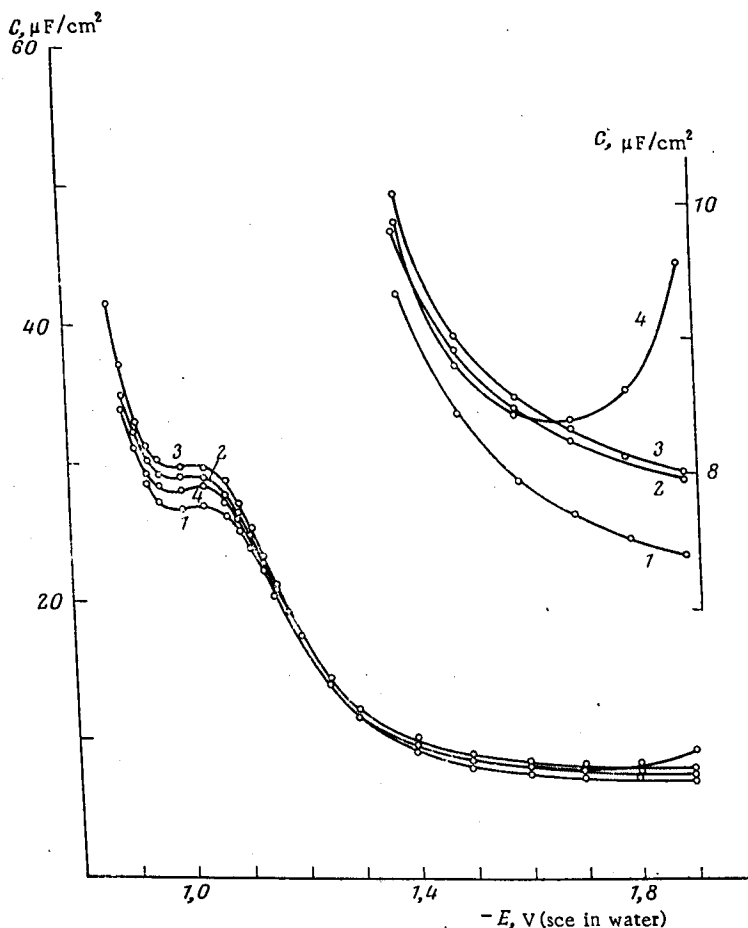


Fig. 3. The C-E curves at In-Ga alloy in 0.1 N solutions in DMSO: 1) LiClO₄, 2) NaClO₄, 3) KClO₄, and 4) CsClO₄.

their adsorption should be more pronounced the smaller their radius. This conclusion is in harmony with the data reported in Table 1 for the mercury electrode:

$$[(\Delta E_{Q=0})_{\text{Br}^-}^{\text{DMSO}} - (\Delta E_{Q=0})_{\text{Br}^-}^{\text{H}_2\text{O}}] \gg [(\Delta E_{Q=0})_{\text{I}^-}^{\text{DMSO}} - (\Delta E_{Q=0})_{\text{I}^-}^{\text{H}_2\text{O}}].$$

At the electrode of eutectic In-Ga alloy, the quantity $\Delta E_{Q=0}$ in solutions of Br⁻ ions increases as one goes from water to DMSO, just as at Hg, but only by a small amount (0.01 V), whereas in solutions of I⁻ ions it decreases by 0.07 V. This result is in qualitative agreement with the ideas as to how adsorption is influenced by the specific interaction of the solvent with the electrode metal. The interaction of DMSO with Hg [4] and with In-Ga alloy [1], which in both cases is stronger than that of water, should provoke a decrease in the adsorbability of different substances from DMSO. This effect turns out to be determining at In-Ga alloy in the case of I⁻, and the adsorption of I⁻ on it decreases as one goes from water to DMSO: $(\Delta E_{Q=0})_{\text{I}^-}^{\text{DMSO}} < (\Delta E_{Q=0})_{\text{I}^-}^{\text{H}_2\text{O}}$. The opposite effect is found in the case of AN: The adsorption of I⁻ ions from AN is increasing strongly, both because of weaker specific interaction of the solvent molecules with the electrode surface [5] and because of lower solvation energy of the anions. In fact, one can see from Table 1 that in AN the quantity $(\Delta E_{Q=0})_{\text{I}^-} = 0.44$ V, which is much higher than in water.

The results of a quantitative investigation of halide ion adsorption on eutectic In-Ga alloy from different solvents will be reported in subsequent communications.

The influence of the cation in solution (Li⁺, Na⁺, K⁺, NH₄⁺) on the value of differential capacity in DMSO had first been studied at the mercury electrode in [4]. Despite the fact that cation solvation in DMSO is stronger than in water [6], the capacity of the mercury electrode at E = const in DMSO increases in the sequence $C_{\text{K}^+} < C_{\text{Na}^+} < C_{\text{Li}^+}$, in accordance with decreasing crystallographic radius of the cation. At the bismuth electrode, an effect of the alkali-metal ion on differential capacity in DMSO has been observed at very negative potentials only. In solutions containing the cations Li⁺, Na⁺, and K⁺, the capacity was governed by the crys-

tallographic radii of the ions, just as at Hg, and was higher only in solutions containing the cations Rb^+ and Cs^+ .

The potential dependence of differential capacity at eutectic In-Ga alloy measured by us in solutions of different alkali-metal cations in DMSO is reported in Fig. 3. It can be seen that at In-Ga, the effect of the cation on the relative values of differential capacity depends on electrode potential. At potentials close to the point of zero charge (the region of the plateaus on the C-E curves of Fig. 3), the capacity increases, as it does in water, in the sequence corresponding to decreasing radius of the solvated cation: $C_{\text{Li}^+} < C_{\text{Na}^+} < C_{\text{K}^+}$. At potentials on the far negative side from the point of zero charge the opposite sequence is found, corresponding to that observed at Hg and Bi: $C_{\text{K}^+} < C_{\text{Na}^+} < C_{\text{Li}^+}$. In solutions containing Cs^+ , the C-E curve occupies an intermediate position, and only at very negative potentials (as at Bi) it is higher than in solutions of all cations studied. The absolute variations of capacity with the cation are small at In-Ga alloy, just as they are at Hg and Bi.

The potential dependence of the relative size of differential capacity at In-Ga alloy in solutions of different cations points to an effect of the electric field of the double layer on the solvation sheath of the cations present in it. One can suggest that the electric field which is increasing as the potential is made more negative relative to the point of zero charge gradually expels the cation's solvation sheath from the compact part of the double layer, and the differential capacity begins to be determined by the ion's crystallographic radius. The special features of the C-E curve at In-Ga alloy in solutions containing Cs^+ ions appear to be due to its specific adsorption [7], just as at Hg.

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