INFLUENCE OF THE METAL ON ELECTRIC DOUBLE-LAYER STRUCTURE IN DIMETHYL SULFOXIDE

I. COMPARISON OF ELECTRIC DOUBLE-LAYER STRUCTURE IN $LiClO_4$ SOLUTIONS ON Hg AND ON EUTECTIC In – Ga ALLOY

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UDC 541.135.52

The structure of the electric double layer on eutectic In – Ga alloy in $LiClO_4$ solutions (from 0.01 to 1 M) in dimethyl sulfoxide (DMSO) has been studied at the dropping electrode by measuring the differential capacity (C) with an ac bridge. Reference electrode was sce in water. It is shown that there is a minimum due to diffuseness of the electric double layer in dilute $LiClO_4$ solutions on the $C - \varphi$ curves. It was verified that the Gouy – Chapman theory is applicable to the In – Ga electrode in DMSO. At $\varepsilon < -9\ \mu C/cm^2$, $C_H^{In\text{-}Ga} = C_H^{Hg}$, but at $\varepsilon > -9\ \mu C/cm^2$, $C_H^{In\text{-}Ga} > C_H^{Hg}$. The potential differences between In – Ga and Hg at different values of charge $(\Delta\varphi^{In\text{-}Ga\text{-}Hg})_\varepsilon$ were compared. At $\varepsilon = 0$, $\Delta\varphi^{In\text{-}Ga\text{-}Hg} = 0.63\,V$, but at $\varepsilon < -9\ \mu C/cm^2$, $\Delta\varphi^{In\text{-}Ga\text{-}Hg} = 0.43\ V$. It was concluded that at $\varepsilon = 0$, the DMSO dipoles are pointing with their negative (oxygen) end toward the In – Ga surface. The $(\Delta\varphi^{In\text{-}Ga\text{-}Hg})_\varepsilon$ values at $\varepsilon = 0$ were compared in different solvents: acetonitrile (AN), water, and DMSO. It is shown that $(\Delta\varphi^{In\text{-}Ga\text{-}Hg})_\varepsilon$ decreases in the series DMSO > H_2O > AN. It is suggested that the interaction between electrode metal and solvent decreases in the same sequence.

Investigations of recent years have shown that in any given solvent, the structure of the compact part of the electric double layer near the potential of zero charge substantially depends on the electrode material, owing to specific interaction between the electrode metal and the solvent molecules. This effect was first discovered in aqueous solutions with Hg and liquid Ga as the example [1].

It was to be expected that the relative values of the electric double-layer parameters of metals in the region of solvent adsorption would change as one goes from one solvent to another. This conclusion was confirmed when electric double-layer structure in acetonitrile (AN) was compared on Hg, Ga, and eutectic In – Ga alloy. It was shown in [2, 3] that in AN one has $C^{Hg} < C^{In\text{-}Ga} \simeq C^{Ga}$ at $\varepsilon = 0$ (ε is the electrode charge), while in water $C^{Hg} < C^{In\text{-}Ga} < C^{Ga}$ (C is differential capacity). The difference in zero-charge potentials between Hg and In – Ga alloy and between Hg and Ga became smaller when going from water to AN, and became more similar to the potential differences between these metals at equal, high negative charge. It followed from the data obtained that AN is less strongly interacting with the electrodes studied than water. Accordingly, the identity of the metal is less important for the structure of the interface. In the case of Ga and eutectic In – Ga alloy, practically the same structure of the electric double layer was found in AN.

Electric double-layer structure on eutectic In – Ga alloy in dimethylsulfoxide (DMSO) was studied in the present work. The structure of the double layer on Hg in DMSO was previously studied by Payne [4]. However, since in comparing electrochemical parameters at different electrodes one must have data obtained relative to the same reference electrode, and the potential drop across the interface between DMSO and the aqueous solution of the reference electrode is not known (and may change depending on the conditions under which the two liquids are brought into contact), the data of [4] could not be used directly,* and a number of measurements on Hg were repeated by us. The sce in water served as reference electrode in our measurements.

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*The nce in water served as the reference electrode in [4].

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 1, pp. 64-68, January, 1977. Original article submitted May 12, 1975.

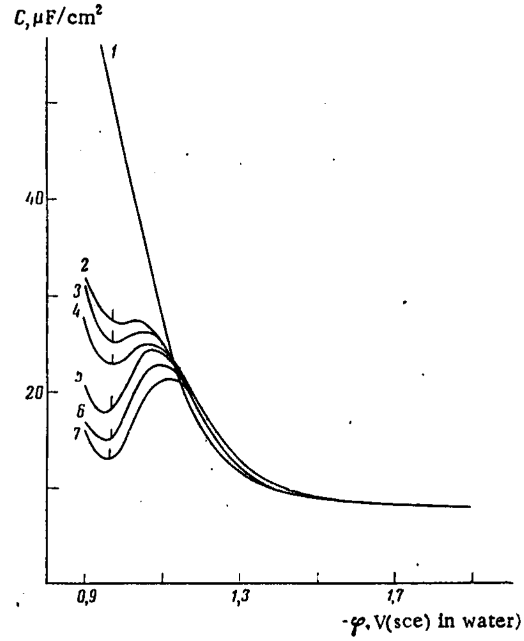

Fig. 1. C – φ curves on In – Ga alloy in $LiClO_4$ solutions in DMSO, at different $LiClO_4$ concentrations: 1) 1.0 M; 2) 0.1 M; 3) 0.07 M; 4) 0.05 M; 5) 0.022 M; 6) 0.014 M; 7) 0.01 M. Strokes mark the $\varphi_{\varepsilon=0}$ values determined from the potential of the open-circuit streaming electrode.

As a solvent, DMSO is of interest because the oxygen atom in its molecule is in a state which is close to ionic, and therefore has high chemical activity [5].

The investigation was carried out by measuring the differential capacity with an ac bridge at dropping electrodes. The zero-charge potential, $\varphi_{\varepsilon=0}$, both on In – Ga and on Hg was determined from the position of the minimum on the differential capacity curves in dilute electrolyte solutions and in addition from the value of potential of a streaming electrode at open circuit where the rate of metal flow was such that a further increase in flow rate had no effect on the potential being measured. The $\varphi_{\varepsilon=0}$ values determined by these two methods in any one solution were in good agreement. The salt $LiClO_4$ was chosen as the electrolyte, since the ClO_4^- anion has low surface activity both on Hg and on In – Ga. This condition is important when one studies the effect of the solvent on the structure of the electric double layer's compact part.

"Chemically pure" ["kh.ch."] grade DMSO was prepurified by freezing-out at 10°C (the melting point of DMSO is 18°C), then it was distilled under reduced pressure (3-5 mm Hg and 42-43°C; at atmospheric pressure, DMSO boils at 189°C). "Very pure ["o.ch."] grade CaO freshly calcined at 1000°C was introduced for two days into the DMSO thus prepurified in order to remove the water, whereupon the DMSO was again distilled under reduced pressure, and directly filled into ampules which were sealed. The water content in DMSO thus purified when determined by the Karl Fischer method was not above 0.01 wt. %. Just before the measurements the DMSO was additionally purified with activated carbon by the method described in [6]. The $LiClO_4$ salt used was thrice recrystallized from aqueous solution, dried at 150°C while continuously being evacuated with a pre-evacuation pump, and kept in fused, evacuated ampules. The In – Ga alloy was prepared as in [7] by dissolving

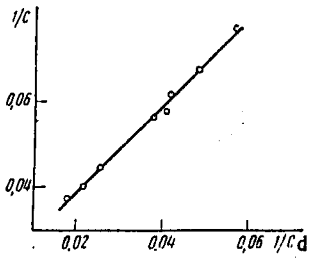

Fig. 2. Plot of $1/C$ vs $1/C_d$ on In – Ga alloy in $LiClO_4$ solutions in DMSO at $\varepsilon = 0$.

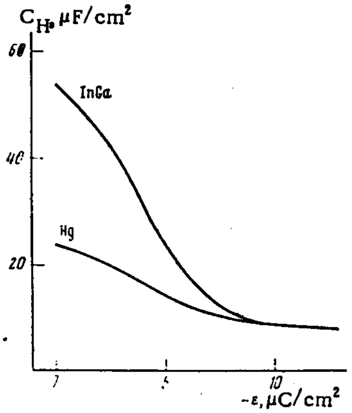

Fig. 3

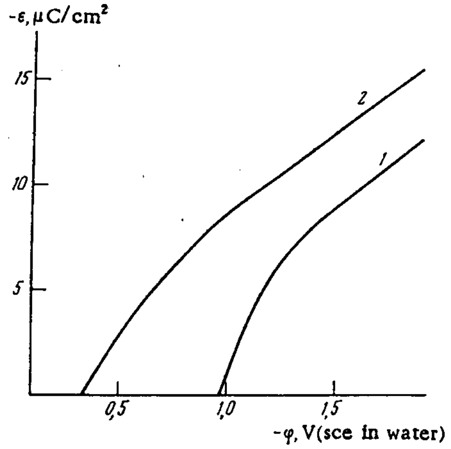

Fig. 4

Fig. 3. C_H as a function of ε in $LiClO_4$ solutions in DMSO on In – Ga and on Hg.

Fig. 4. The ε – φ curves on In – Ga alloy (1) and on Hg (2) in 0.1 M $LiClO_4$ in DMSO.

metallic In in Ga beneath a weak alkali solution. The purity of the Ga used was 99.9999% ["GL-v.ch.," "highly pure" grade], that of the In was 99.9998% ["In-os.ch.-19-3," "specially pure" grade]. The measurements were conducted at 32°C.

The C – φ curves for In – Ga in $LiClO_4$ solutions of different concentrations are reported in Fig. 1.

The differential capacity curves measured by us on Hg were in full agreement with the C – φ curves reported in [4]. When comparing the data obtained in [4] with those of the present work the potential of the mercury electrode was expressed relative to the zero-charge potential of Hg in the test solution.

Using the results reported in Fig. 1 we tested the applicability of the Gouy – Chapman theory to In – Ga in DMSO. The slope of the plot of $1/C$ vs $1/C_d$ in $LiClO_4$ solutions of different concentration at $\varepsilon = 0$ was found to be unity (Fig. 2). In calculating the capacity of the diffuse part of the electric double layer, C_d, we used the bulk value, 46.7, of the dielectric permittivity of DMSO. Applicability of the Gouy – Chapman theory to the Hg electrode in DMSO was first demonstrated in [4].

Values of the capacity of the electric double layer's compact part, C_H, at different values of electrode charge are compared in Fig. 3 for In – Ga and Hg in DMSO. It can be seen that at $\varepsilon = 0$, $C_H^{In-Ga} \gg C_H^{Hg}$, while at high negative values of charge the C_H on In – Ga and on Hg are the same. The inequality at $\varepsilon = 0$ indicates that the DMSO interacts more strongly with In – Ga alloy than with Hg.

The ε – φ curves on In – Ga and on Hg in 0.1 M $LiClO_4$ which were calculated by integrating the C – φ curves measured in the same solution are reported in Fig. 4. The zero-charge potentials of In – Ga and Hg in 0.1 M $LiClO_4$ were determined from the values of potential of open-circuit streaming electrodes. It can be seen from Fig. 4 that the difference in zero-charge potentials between In – Ga and Hg in DMSO is 0.20 V larger than the potential difference between these electrodes at high negative values of charge. After comparing the ε – φ curves on In – Ga alloy and Hg in DMSO one can conclude that at zero charge the DMSO dipoles

TABLE 1. Values of C_H (μF/cm²) on In – Ga and Hg in Various Solvents at ε = const

Solvent	ε	C_H on electrode of		c_H^{In-Ga} / c_H^{Hg}
		In-Ga	Hg	
AN	0	28,5	16	1,8
	≪0	10	10	1
H_2O	0	60,5	29	2,1
	≪0	18	17	1,05
DMSO	0	54	24	2,25
	≪0	8.5	8,5	1

TABLE 2. The Potential Differences between In – Ga and Hg Electrodes

Me_1—Me_2	Solvent	$(\Delta\varphi^{In\text{-}Ga\text{-}Hg})_{\varepsilon=0}$, V	$(\Delta\varphi^{In\text{-}Ga\text{-}Hg})_{\varepsilon<0}$, V
In-Ga–Hg	AN	0,42	0,37
	H_2O	0,48	0,35
	DMSO	0,63	0,43

(just as the water dipoles) are pointing with their negative (oxygen) end toward the surface of the In – Ga electrode. This conclusion is in harmony with the presence of a semipolar bond between oxygen and sulfur in the DMSO molecule.

The C_H values on In – Ga and on Hg at $\varepsilon = 0$ and at equal, high negative values of charge where the structure of the electric double layer is independent of the electrode metal* and also the ratios $(C_H^{In\text{-}Ga}/C_H^{Hg})$ in different solvents: AN, water, and DMSO are compiled in Table 1; values for the potential differences between these electrodes in the same solvents at $\varepsilon = 0$ and at $\varepsilon \ll 0$ are given in Table 2.†

It can be seen from Table 1 that at $\varepsilon = 0$, C_H on In – Ga is always larger than C_H on Hg, while at high negative values of charge in the same solvent, the C_H values on In – Ga and on Hg coincide. The ratio $(C_H^{In\text{-}Ga}/C_H^{Hg})_{\varepsilon=0}$ increases as one goes from AN to water and further to DMSO. The difference between the zero-charge potentials of In – Ga and Hg increases in the same series (Table 2). Thus, the value of $(\Delta\varphi^{In\text{-}Ga\text{-}Hg})_{\varepsilon=0}$ became 0.21 V larger on going from AN to DMSO.

It follows from the data reported that the specific interaction of the present solvents with the electrode is always more pronounced in the case of In – Ga than in the case of Hg, and increases in the sequence AN < H_2O < DMSO.

It must be noted that at high negative values of charge, the potential difference between In – Ga and Hg depends much less on the solvent than at $\varepsilon = 0$ (Table 2). This observation agrees with the concepts developed by Frumkin [8], which say that the potential difference between metals at ε = const will be close to the difference in work functions when the potentials are measured in a region where the electric double-layer structure is independent of electrode material.

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*In water and at high negative values of charge, $C_H^{In\text{-}Ga} > C_H^{Hg}$, but the ratio $(C_H^{In\text{-}Ga}/C_H^{Hg})$ is independent of charge [2]. It has not been elucidated why at high negative values of charge the values of capacity on In – Ga are a little higher than on Hg in water.

† In calculating the potential difference between In – Ga and Hg in water we introduced a correction for unequal electric double-layer structure at these electrodes at high negative values of charge by multiplying the experimental ε values for In – Ga by $(C_H^{Hg}/C_H^{In\text{-}Ga})_{\varepsilon\ll 0} \simeq 0.9$ [2].