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EFFECT OF THE SPECIFIC INTERACTION OF A SOLVENT WITH ELECTRODE METAL ON THE STRUCTURE OF THE ELECTRIC DOUBLE LAYER AND ADSORPTION

I. A. Bagotskaya, N. B. Grigor'ev, and L. M. Dubova

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It was shown that the specific interaction of a solvent with a metal is accompanied by a change of the differential capacitance of the electric double layer, the zero-charge potential, and the adsorption of the electrode determined on the basis of an analysis of experimental data obtained on mercury, liquid gallium, and a eutectic alloy of indium and gallium, which is similar in its electrochemical properties to indium, as well as on other metals which weakly adsorb hydrogen in aqueous, acetonitrile, and dimethyl sulfoxide solutions.

The effect of the specific interaction of a solvent with a metal electrode on the structure of the electric double layer and adsorption was first discovered by comparing the structure of the electrode/solution phase boundary on liquid gallium and mercury in aqueous solutions [1, 2]. The stronger interaction of the oxygen atom of the water molecule with gallium relative to mercury leads to the orientation of some of the water molecules on gallium towards the electrode surface by the negative oxygen end at some not very negative charge Q (in contrast, at this charge, the water molecules on mercury are oriented with the positive end of the dipole towards the electrode surface). As the negative charge decreases, the amount of the water molecules oriented in this fashion on galliums which are specifically oriented increases. For the compensation of the increasing adsorption (dipole) potential jump of water, an additional loss of electric charge is required and the differential capacitance of the gallium electrode is found higher than for the mercury electrode. In 1 N Na_2SO_4 at zero-charge potential $\varphi_{Q=0}$, the capacitance of the double layer on gallium reaches 135 $\mu F/cm^2$ and is ~4 times greater than on mercury. At large negative charges corresponding to identical orientation of water molecules on gallium and mercury (the positive end of the dipole towards the surface), the values for the differential capacitance coincide.

The different specific adsorption of water molecules on gallium and mercury leads to a significant difference in the zero-charge potential of these metals equal to 0.51 V from the difference of the work function between them, the value of which, according to literature data, corresponds to 0.20 [3], 0.16 [4], and 0.15 V [5]. With increasing negative charge of the surface, the difference in potentials between gallium and mercury at the same charge $\Delta\varphi_Q^{Ga-Hg}$ initially decreases and then becomes constant, equal to 0.17 V and is close to the difference in work functions of these metals. The value $\Delta\varphi_{ads\ H_2O}^{Ga-Hg} = \Delta\varphi_{Q=0}^{Ga-Hg} - \Delta\varphi_{Q\ll 0}^{Ga-Hg} = 0.34$ V corresponds to the difference in the adsorbed potential jumps of water on gallium and mercury at Q = 0.

Subsequently, differences in the structure of the electric double layer were also found on other metals which weakly adsorb hydrogen: lead [6], cadmium [7], indium [8], an In–Ga eutectic alloy [9],* tin [11], bismuth

*In the In–Ga system, indium is the surface-active component [10] and the In–Ga eutectic alloy in its electrochemical properties is similar to pure indium [8]. At room temperature, this alloy is in the liquid state and a number of difficulties are eliminated in working with this alloy which are characteristic of solid electrodes.

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[12], and zinc [13]. At sufficiently negative charges, the values of the capacitance of the dense part of the double layer C_Γ on these metals are similar. With a shift in Q towards less negative values, values of C_Γ increase and begin to depend on the nature of the metal. At Q = 0, $C^{Ga} > C_\Gamma^{In-Ga} > C_\Gamma^{Cd} > C_\Gamma Sn > C_\Gamma^{Pb} > C_\Gamma^{Hg} > C_\Gamma^{Bi}$. Trasatti [14] has indicated a correlation between the heat of formation of the metal oxide phase and the magnitude of the adsorption potential jump of water on the metal.

There have been a number of attempts to provide a quantitative description of the effect of the specific adsorption of water on the structure of the electric double layer [15]. The specific adsorption of water affects the adsorption properties of the electrodes. This is most easily seen for aliphatic alcohols, the adsorption energies of which in the first approximation are determined by the repulsion of the alcohol molecules from the solution bulk to the phase separation boundary. Since the adsorption of alcohols is accompanied by desorption of water molecules and the adsorption of water depends on the nature of the metal, then in the potential region, in which water is adsorbed specifically on the electrode, the effective adsorption energy of alcohols must be determined by the degree of affinity of the metal electrode towards water, i.e., its hydrophilicity:

	B_a, liters/mole		B_b, liters/mole
Hg	40 [16]	Sn	27 [19]
Bi	28 [17]	In-Ga alloy	17 [20]
Pb	22 [18]	Cd	11 [21] .

The above data for $n\text{-}C_5H_{11}OH$ indicate that the values of the adsorption equilibrium constants B_0 on various metals calculated according to the Frumkin–Damaskin theory of organic compounds and, thus, the standard free energy of adsorption of $n\text{-}C_5H_{11}OH$, decreases in going from mercury to the In–Ga eutectic alloy and cadmium; bismuth, lead and tin, in their values of B_0, occupy an intermediate position. Corresponding data for gallium are lacking in the literature. The series obtained for change in B_0 qualitatively corresponds to an increase in the hydrophilicity of these metals in the same sequence. The values for C_Γ resulting from the specific adsorption of water increase in going from mercury to lead, tin, cadmium and then, to the In–Ga alloy.*

In the region of potentials corresponding to identical orientation of water molecules on the various electrodes, alcohol desorption should take place at the same potential jump in the electric double layer independent of the nature of the electrode metal. However, with specific adsorption of water, the term $(\varphi - \varphi_{Q=0})$ is not an index of the drop in potential in the double layer. This produces a situation in which at 0.1 M $n\text{-}C_5H_{11}OH$ concentration, at which the negative alcohol desorption peaks occur in the potential region corresponding in, the first approximation, to identical structure of the double layer on the various metals, the term $(\varphi_{peak} - \varphi_{Q=0})$ is a function of the degree of hydrophilicity of the metal. With increasing hydrophilicity of the metal, $|\varphi_{peak} - \varphi_{Q=0}|$ decreases [23]. For example, on gallium $|\varphi_{peak} - \varphi_{Q=0}|$ corresponds to 0.32 V, while it is 0.55 V on cadmium and 0.74 V on mercury. In addition, the magnitude of the electrode charge which characterizes the potential drop in the double layer at the peak potential both in the background solution and in the presence of n-amyl alcohol hardly depends on the nature of the metal: In the base electrolyte solution $Q_{peak} = -13.3 \pm 1.0\ \mu C/cm^2$ and in the presence of the alcohol, $-8.7 \pm 0.7\ \mu C/cm^2$ [23].

It should be expected that in going from water to other solvents, the ratios between the parameters of the electric double layers of metals in the region of solvent adsorption will change. From Table 1, in which we list values of C_Γ and potential difference between mercury and the In–Ga eutectic alloy in three solvents (water, acetonitrile [24], and dimethyl sulfoxide (DMSO) [25]) at various charges, it is seen that C_Γ at Q = 0 on the alloy is always greater than on mercury. The ratio $C_\Gamma^{In-Ga}/C_\Gamma^{Hg}$ depends on the nature of the solvent and increases in going from acetonitrile to water and then to DMSO. In this series, the term $(\Delta\varphi_{Q=0}^{In-Ga-Hg})$ also increases. Thus, in going from acetonitrile to DMSO, the value for $(\Delta\varphi_{Q=0}^{In-Ga-Hg})$ increases by 0.21 V. The data presented indicate that the specific interaction of the solvents studied with electrodes in the case of In–Ga is always more pronounced than in the case of mercury and increases in the series acetonitrile < water < DMSO. At $Q \ll 0$, $C_\Gamma^{In-Ga}/C_\Gamma^{Hg} \approx 1$ and the value of $(\Delta\varphi_Q^{In-Ga-Hg})$ depends much less on the nature of the solvent and, according to Frumkin, is similar to the difference in work functions.

For gallium, data on the structure of the double layer in nonaqueous solutions are available only for acetonitrile [26]. In a nonactive electrolyte solution in acetonitrile, the term $\Delta\varphi_{Q=0}^{Ga-Hg} = 0.29$ V and is 0.21 V less than in water. The value for $\Delta\varphi_{Q\ll0}^{Ga-Hg}$ in acetonitrile corresponds to 0.23 V and is only 0.06 V less than in water.

*The discrepancy in the values of B_0 and C_Γ at small negative charges and at Q = 0 on lead, tin, and cadmium is apparently related to insufficient accuracy in the determination of these values on the solid metals, in particular, due to their crystallographic nonuniformity [22].

TABLE 1. Values of C_Γ and Potential Differences of In–Ga Alloy and Mercury in Three Solvents at Various Charges

Parameters	C_Γ, μF/cm² at Q=const					
	AH		H_2O		DMSO	
	Q=0	Q≪0	Q=0	Q≪0	Q=0	Q≪0
In-Ga	28,5	10	60,5	18	54	8,5
Hg	16	10	29	17	24	8,5
$C_\Gamma^{In\text{-}Ga}/C_\Gamma^{Hg}$	1,8	1,0	2,1	1,05	0,63	1,0
$(\Delta\varphi_Q^{In\text{-}Ga-Hg})$, V	0,42	0,37	0,48	0,35	2,25	0,43

TABLE 2. Values of the Adsorption Potentials of Halide Anions on Mercury and In–Ga Alloy in Various Solvents

Electrode	$\Delta\varphi_{Q=0}^{Hal^-}$	Solvent, halide concn. was 0.1 N		Reference
		DMSO	H_2O	
Eutectic alloy	$\Delta\varphi_{Q=0}^{Br^-}$	0,07	0,06	[27]
In-Ga	$\Delta\varphi_{Q=0}^{I^-}$	0,07	0,14	[27]
Hg	$\Delta\varphi_{Q=0}^{Br^-}$	0,17	0,10	[28]
	$\Delta\varphi_{Q=0}^{I^-}$	0,27	0,26	[28]

Note. In our earlier work [24], $\Delta\varphi_{Q=0}^{I^-} = 0.44$ V.

The effect of the specific interaction of the solvent with the electrode on the adsorption of surface-active anions [27] may be followed qualitatively by comparison of the adsorption potentials of Br^- and I^- ($\Delta\varphi_{Q=0}^{Hal^-}$, Table 2) on mercury and the In–Ga alloy in various solvents.

It is seen from the table that the effect of the nature of the solvent on term $\Delta\varphi_{Q=0}^{Hal^-}$ in a solution of the same anion depends on the nature of the metal. On mercury, replacing water by DMSO leads to an increase in $\Delta\varphi_{Q=0}^{Hal^-}$ and, thus, of the anion adsorption.*

It is known that the solvation energy of anions in protic solvents decreases with increasing radius of the anion, while, on the other hand, in aprotic solvents, this term increases. As a consequence, the effect of the solvation energy on their adsorption in going from water to DMSO should be more pronounced with decreasing radius of the anion. This conclusion is consistent with the data in Table 2 for Hg: $|(\Delta\varphi_{Q=0}^{Br^-})_{DMSO} - (\Delta\varphi_{Q=0}^{Br^-})_{H_2O}| \gg |(\Delta\varphi_{Q=0}^{I^-})_{DMSO} - (\Delta\varphi_{Q=0}^{I^-})_{H_2O}|$. On the In–Ga alloy, the value for $\Delta\varphi_{Q=0}^{Hal^-}$ in a bromide anion solution increases in going from water to DMSO, as in the case on mercury, though by a small amount (0.01 V), while the value decreases for a solution of the iodide ion by 0.07 V. The result obtained corresponds qualitatively with an effect of the specific interaction of the solvent with the electrode on adsorption. The interaction of DMSO, which is stronger than the interaction of water both with mercury [28] and the alloy [25], should facilitate a decrease in the adsorption of various species from DMSO. Thus, $|(\Delta\varphi_{Q=0}^{I^-})_{DMSO}| < |(\Delta\varphi_{Q=0}^{I^-})_{H_2O}|$. In acetonitrile, as a result of the weakening of the specific interaction of the solvent with the electrode and decrease in the solvation energy of anions, the adsorption of I^- anions in going from water to acetonitrile increases and on the In–Ga alloy, $\Delta\varphi_{Q=0}^{I^-} = 0.44$ V.

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EFFECT OF ADSORBED GASES ON THE SURFACE PROPERTIES OF METALS

R. Kh. Burshtein, N. A. Shurmovskaya, T. V. Kalish, and L. A. Larin

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Data are given on the determination of the work function of various metals (Hg, Ag, Pb, Ga, Fe, Pt) and its response to chemisorbed oxygen and water vapor. We examined the mechanism for the initial reaction stage of the metals with oxygen and compared the different work functions and zero charge potentials of each of the metals with respect to the effect of adsorbed water.

Chemisorbed gases on metals change the work function and affect the electrochemical and catalytic properties of a metal. From the theory of the electric double layer at the metal/solution interface developed by Frumkin [1], it follows that the zero charge potential difference ($\Delta\varphi_{E=0}$) between two metals is close to their Volta potential in a vacuum, i.e., $W_1 - W_2 = (\varphi_1 - \varphi_2)_{E=0}$. In this regard, however, we do not consider the surface dipoles which may arise in electrochemical systems during the chemisorption of water at the metal/solution interface [2].

Investigations on the adsorption of oxygen on iron [3] and nickel [4] by the method of contact potential difference (c.p.d.)* has given information on the mechanism of the initial stages of metal oxidation. With chemisorption of oxygen on iron the value and sign of the c.p.d. are determined by the amount of adsorbed oxygen and the temperature of the reaction between the adsorbate and the adsorbent. Oxygen adsorbed on iron at −120°C increases the work function. At 100°C the contact potential changes not only in amount but also in sign.

The change in ΔW upon heating Fe with the same amount of adsorbed oxygen ($2 \cdot 10^{15}$ molecules O_2/cm^2) on the surface at a temperature of 20-300°C is indicated by the relationship shown in Fig. 1a [5]. At 23°C ΔW

*The contact potential (ΔW) with a minus sign corresponds to a work function decrease and with a plus sign to a work function increase.

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