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The Influence of the Nature of the Metallic Phase on the Structure of the Electrical Double Layer and the Kinetics of the Evolution of Hydrogen

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The influence of the crystallographic structure of the surface of a solid electrode and of the specific interaction between the solvent and the metal on the properties of the electrical double layer and the adsorption of ions and dipolar molecules on metals which do not adsorb hydrogen is examined. The problem of the influence of the structure of the electrical double layer on the kinetics of the evolution of hydrogen on bismuth, tin, lead, and cadmium, in acid and alkaline solutions is discussed.
The bibliography includes 80 references.

CONTENTS

I. Introduction 965
II. The influence of the crystallographic structure of the electrode surface on the properties of the electrical double layer and on adsorption 966
III. The influence of the nature of the metal and the chemisorption of solvent molecules on the structure of the interface 967
IV. The influence of the structure of the electrical double layer on the kinetics of the cathodic evolution of hydrogen 969

I. INTRODUCTION

Significant progress has been achieved in the last decade in quantitative studies of the structure of the electrical double layer, adsorption phenomena, and the laws governing the occurrence of electrochemical reactions on electrodes made of a wide variety of different metals. Metals on which conditions of ideal polarisability can be achieved to a satisfactory degree of approximation over a wide range of potentials φ are the most suitable for a quantitative test of the theoretical concepts concerning the structure of the electrode/solution interface[1-4]. In contrast to mercury, on solid electrodes a fundamentally new problem involves the study of the influence of the crystallographic characteristics of the surface of the metal on the structure of the electrical double layer, particularly its dense component (together with the problem of the influence of the chemical nature of the metal). The investigation of the structure of the interface on different faces of a single crystal is most promising in this sense.

Frumkin and coworkers[5,6] showed that one of the most exact methods for the study of the structure of the electrical double layer involves the measurement of the variation of the differential capacitance C with φ. However, in the measurement of the capacitance of solid metals it is necessary to eliminate the sources of the false frequency dispersion of the capacitance (roughness of the surface, the phenomenon of saturation, etc.)[3,4,7,8]. A number of methods for smoothing the surfaces of test electrodes have now been developed and successfully applied.

Frumkin and coworkers[9] showed that surface fusion of the metal constitutes a promising method for the preparation of solid electrodes with the roughness coefficient of the surface close to unity. A special procedure for the preparation of drop-shaped surface-fused electrodes with a smooth surface has been developed in the Electrochemical Laboratory at the Tartu State University[10,11]. Subsequently the procedure was used to prepare drop-shaped antimony[12], tin[13], and cadmium[14] electrodes. Fig. 1 shows that the variation of $1/C$ with the reciprocal of the diffuse layer capacitance $1/C_d$ of bismuth can be represented over a wide range of KF concentrations (0.001–2 M) and for different surface charges ϵ by straight lines with an average reciprocal of the slope of 1.01–1.02.[15] It has been shown[16] that the slope of the linear plot of $1/C$ against $1/C_d$ for $\epsilon = 0$ differs from unity by less than 10% in the case of antimony. These results show that surface-fused electrodes have a perfectly smooth surface.

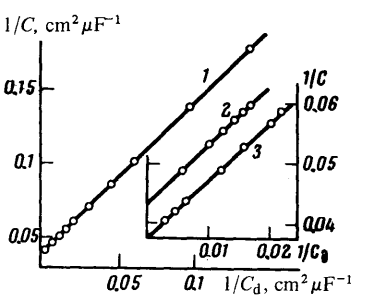


Figure 1. Variation of the reciprocal of the differential capacitance $1/C$ with the reciprocal of the capacitance of the diffuse layer $1/C_d$ in the range of KF concentrations from 0.001 to 2.0 M for different values of ϵ (C cm^{-2}): 1) 0; 2) −3; 3) +2.

Among solid electrodes, bismuth is the metal which exhibits the widest (after mercury) range of ideal polarisability potentials in both aqueous[10,15] and non-aqueous[17-19] media. On the other hand, many of the physical and chemical properties of bismuth differ significantly from those of mercury and metals resembling it, and lead to its classification as a semimetal. Bismuth is therefore an

interesting object of study for the elucidation of the influence of the nature of the metallic phase and also of the crystallographic structure of the surface on the double layer parameters and adsorption. In this review attention is concentrated on the following problems in relation to bismuth together with the relevant data for other electrodes:

(1) the influence of the crystallographic structure of the electrode surface on the characteristics of the double layer and on the adsorption of molecules and ions;

(2) the influence of the nature of the metal and of the chemisorption of solvent molecules (particularly water) on the structure of the interface and on adsorption;

(3) the dependence of the characteristics of the cathodic evolution of hydrogen on the nature of the metal and the structure of the double layer.

II. THE INFLUENCE OF THE CRYSTALLOGRAPHIC STRUCTURE OF THE ELECTRODE SURFACE ON THE PROPERTIES OF THE ELECTRICAL DOUBLE LAYER AND ON ADSORPTION

The vast majority of the literature data concerning the structure of the electrical double layer and adsorption on solid metals refer to electrodes with a polycrystalline surface. Measurements on individual faces of a single crystal are associated mainly with the determination of the zero-charge potential $\varphi_{\epsilon=0}$ of the face. The characteristics of the adsorption of ions and molecules on single crystal faces have been studied quantitatively on zinc[20,21], bismuth[22], gold[23], and silver[24]. Nevertheless the experimental data which have accumulated indicate an appreciable influence of the crystallographic characteristics on the double layer parameters. It has been established in studies on zinc[20,21,25] and bismuth[26-30] that the role of the nature of the polycrystallinity of the surface is manifested particularly clearly in the adsorption of organic compounds with a powerful attraction interaction in the adsorption layer.

In the study of the adsorption of pyridine[26], certain aliphatic ketones[27], esters[28], and camphor[29] on a surface-fused bismuth electrode the phenomenon of the splitting of adsorption–desorption maxima has been observed (Fig. 2). Such phenomena, which have been noted in many instances also on the polycrystalline surface of zinc[20,21,25], are absent from the homogeneous mercury surface and the (111) face of a bismuth single crystal. According to data for bismuth, the adsorption of pyridine and the majority of the ketones and esters investigated is accompanied by the splitting of the cathodic maxima into two, which is more pronounced the higher the concentration of the organic substance in solution. There are actually three peaks on the C–φ curves for propyl acetate solutions. The anodic maxima, which are obtained only for bismuth among solid metals, exhibit a smaller tendency towards splitting; the splitting of the anodic peaks into two components has been observed only for the adsorption of propyl acetate[28] and camphor[29] on bismuth.

As for the zinc electrode, the splitting of the adsorption maxima on bismuth is due to the polycrystallinity of the electrode, the surface of which comprises faces with different crystallographic indices. The individual narrow peaks in the region of the adsorption–desorption maxima (Fig. 2) describe the desorption of organic molecules from different single crystal faces, one of which is the (111) face. Presumably the difference between the values of $\varphi_{\epsilon=0}$ on different single crystal faces is the main factor among several responsible for the splitting of the maxima. The value of $\varphi_{\epsilon=0}$ for the basal (111) face of the bismuth single crystal in potassium sulphate solution is −0.68 V relative to the saturated calomel electrode[31], i.e. it is more negative by 30 mV than $\varphi_{\epsilon=0}$ for a surface-fused electrode[10,32]. On the basis of the value of $\varphi_{\epsilon=0}$ for the (111) face, the values of $\varphi_{\epsilon=0}$ for the remaining two faces involved in adsorption measurements can be estimated approximately from the peak potentials. $\varphi_{\epsilon=0}$ for the face corresponding to the first, i.e. least cathodic, peak of the split propyl acetate maximum is between −0.62 V and $\varphi_{\epsilon=0}$ for the face corresponding to the middle peak is in the range between −0.63 and −0.65 V.[30] However, it must be emphasised that the values quoted are merely approximate and do not permit the identification of the face.

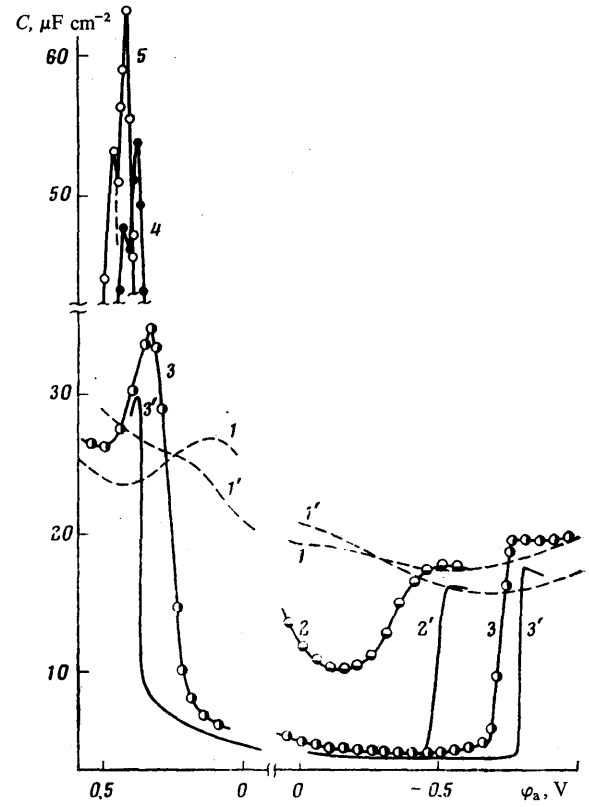


Figure 2. Differential capacitance curves for bismuth (curves *1* and *5*) and mercury (curves *1′* and *3′*) in 0.1 M NaF (bismuth and mercury) and $HClO_4$ (bismuth) solutions with added camphor; camphor concentration (M): 1) and 1′) 0; 2) and 2′) 2×10^{-4}; 3) and 3′) 1.5×10^{-3}; 4) 5×10^{-3}; 5) 7×10^{-3} (the potentials are given relative to the zero-charge point).

Electron-diffraction analysis has established that the splitting of the adsorption maxima is favoured by the macroscopic nature of the crystallographic heterogeneity of the surface of the bismuth electrode, characterised by

the presence on the surface of relatively large single-crystal sections[28-30]. The highly developed polycrystallinity and the associated appreciable energy inhomogeneity promote the manifestation of a broad spectrum of interactions in the adsorption layer, which leads to the spreading of the maxima and not to their splitting[25,30]. Mathematical analysis of electron diffraction patterns showed that, on a completely smooth bismuth surface produced by surface fusion (characterised by greatly extended reflections), there are relatively large single-crystal regions with the Miller indices (100), (101), (111), and (211).[30] Together with macroscopic single-crystal planes, one sometimes encounters aggregates of single crystals comprising between two and four crystallites with the indices (100), (111), (101), (552), (321), etc. Statistical treatment of the electron-diffraction data showed that the surface of the surface-fused bismuth drop comprises mainly two–three distinct single-crystal faces (the fraction of the total drop surface corresponding to them is about 80–90%). The crystallographic structure of the surface produced by partial fusion is statistically reproducible in different experiments owing to the stability of the conditions employed in the preparation of bismuth electrodes[10,11].

III. THE INFLUENCE OF THE NATURE OF THE METAL AND THE CHEMISORPTION OF SOLVENT MOLECULES ON THE STRUCTURE OF THE INTERFACE

Frumkin and coworkers[33,34] showed for the first time that the influence of the nature of the metal on the structure of the double layer and adsorption can be shown very clearly in terms of its hydrophilic properties. In particular, it has been established that, owing to the strong chemisorption of water molecules, the classical theory of the double layer is inapplicable to the double layer on gallium[35].

According to the literature data, in the region where $\epsilon \geqslant 0$ the adsorption parameters of organic compounds and ions depend markedly on the nature of the metal, owing to both their different hydrophilic properties and to the specific interaction of the functional group in the adsorbate molecule with the electrode surface. Table 1 presents the standard free energies of adsorption ΔG°_{A} of aliphatic alcohols, acids, and ketones, on mercury[36-38] and bismuth[27,39,40]. It is seen that the values of $-\Delta G^{\circ}_{A}$ for the higher members of the homologous series of the above compounds on bismuth are somewhat lower than on mercury. Since the functional group in the molecules of the higher homologues is so remote from the electrode surface that its specific interaction with the electrode may be neglected, the above difference is a result of the difference between the water adsorption energies on bismuth and mercury. Comparison of the values of $-\Delta G^{\circ}_{A}$ for different compounds shows that the energy of adsorption of water molecules on bismuth is on average 0.3–0.4 kcal mole^{-1} higher than on mercury. On the other hand, comparison of data for the adsorption of alcohols on bismuth and cadmium[41] shows that the energy of adsorption of water on bismuth is lower by 0.35–0.45 kcal mole^{-1} than on cadmium.

The relatively higher free energies of adsorption of the first members of the homologous series on bismuth compared with mercury are due to the appreciable specific interaction of the oxygen atoms in the functional group with the bismuth surface. The difference between the specific interactions of the functional groups with bismuth and mercury can be characterised by the quantity

$$[(-\Delta G^{0}_{A})_{n=6} - (-\Delta G^{0}_{A})_{n=2}]_{Hg} - [(-\Delta G^{0}_{A})_{n=6} - (-\Delta G^{0}_{A})_{n=2}]_{Bi} = (\Delta\Delta G^{0}_{A}).$$

Table 1 shows that the energy of interaction of the OH group with bismuth is 0.31 kcal mole^{-1} higher and that of the COOH group 0.60 kcal mole^{-1} higher than with mercury. It is interesting to note that the oxygen atoms in water and alcohol molecules interact with the bismuth surface approximately to the same extent. The stronger interaction of the COOH group with the electrode surface compared with the OH group is due to the face that the carboxy-group contains two oxygen atoms. The behaviour indicated by Table 1 has been confirmed also by comparing the adsorption activities of aliphatic compounds on bismuth and on the free surfaces of the solution[27,42,43].

Table 1. Standard free energies of adsorption of aliphatic compounds.

Compound	$(-\Delta G^{0}_{A})_{Hg}$, kcal mole^{-1}	$(-\Delta G^{0}_{A})_{Bi}$, kcal mole^{-1}	$(-\Delta G^{0}_{A})_{Hg} - (-\Delta G^{0}_{A})_{Bi}$, kcal mole^{-1}
C_2H_5OH	1.86	1.87	−0.01
C_3H_7OH	3.05	2.65	0.40
C_4H_9OH	3.83	3.47	0.36
$C_5H_{11}OH$	4.58	4.26	0.32
$C_6H_{13}OH$	5.39	5.09	0.30
$(-\Delta G^{0}_{A})_{n=6} - (-\Delta G^{0}_{A})_{n=2}$*	3.53	3.22	0.31
C_2H_5COOH	3.1	3.3	−0.2
C_3H_7COOH	3.8	3.7	0.1
C_4H_9COOH	4.55	4.4	0.15
$C_5H_{11}COOH$	5.55	5.1	0.45
$C_6H_{13}COOH$	6.3	5.9	0.4
$(-\Delta G^{0}_{A})_{n=6} - (-\Delta G^{0}_{A})_{n=2}$	3.2	2.6	0.6
Ethyl methyl ketone	—	3.55	—
Methyl propyl ketone	4.7	4.3	0.4
Butyl methyl ketone	5.35	5.00	0.35

*n is the number of carbon atoms in the hydrocarbon group.

The adsorption data obtained make it possible to establish a series of surface activities of aliphatic compounds reflecting the interaction of the functional group with the electrode surface. Judging from the values of ΔG°_{A}, the interaction of the functional group with the bismuth surface becomes stronger in the sequence OH < C=O < COOH.[29,44] This sequence reflects the enhancement of the specific interaction between the oxygen atoms and the bismuth surface.

The π-electron interaction between the aromatic ring and the positive surface charges, which should depend in principle on the nature of the metal, is known to play a significant role in the adsorption of aromatic compounds on electrodes. Table 2 presents the values of the adsorption energy gain $-\Delta G_{A}$ on passing from the solution/air interface to the interface with bismuth or mercury for $\Delta\sigma = 0.5$ μJ cm^{-2}.[45] The data in Table 2 show that the adsorption of all aromatic compounds on the bismuth surface is energetically more favourable than on the free surface of the solution. According to the Table, the values of $-\Delta G_{A}$ for mercury are 0.3–1.3 kcal mole^{-1} higher than for bismuth.

As shown above, one of the causes of the increased surface activity of organic compounds on bismuth is a

stronger adsorption of water molecules than on mercury. Together with this, it is necessary to take into account also the semimetallic nature of bismuth, which leads to a weakening of the π-electron interaction between adsorbate molecules and the surface. The energy of the π-electron interaction between the adsorbed molecules of benzene derivatives and an uncharged bismuth surface can be estimated approximately by comparing the values of $-\Delta G_A$ for phenol and cyclohexanol. According to the data in Table 2, the difference between the values of $-\Delta G_A$ for phenol and cyclohexanol (0.7 kcal mole^{-1}) characterises the energy of the π-electron interaction of benzene derivatives; however, depending on the nature and structure as well as the orientation of the adsorbed molecules, this value can vary somewhat. The energy of the additional π-electron interaction when the molecule includes a second benzene ring (naphthalene derivatives) appreciably exceeds the energy of the interaction of the functional group (OH, NH_2, etc.) with the bismuth surface.

Table 2.

Compound	$-\Delta G_A$, kcal mole^{-1}		Compound	$-\Delta G_A$, kcal mole^{-1}	
	Bi	Hg		Bi	Hg
Phenol	1.0	1.8	o-Toluidine	1.5	2.2
Cyclohexanol	0.3	—	Pyridine	0.6	0.9
Catechol	1.8	2.7	Benzene	0	0.5
Hydroquinone	2.8	3.7	Toluene	0.4	0.7
o-Cresol	1.3	—	Naphthalene	2.2	—
Benzyl alcohol	1.3	—	α-Naphthol	3.9	—
Benzoic acid	1.3	1.74	α-Naphthylamine	3.6	—
Aniline	1.2	2.5	α-Naphthoic acid	3.6	—

of which the attraction interaction between the horizontally and vertically oriented molecules on bismuth is much stronger than on mercury[48].

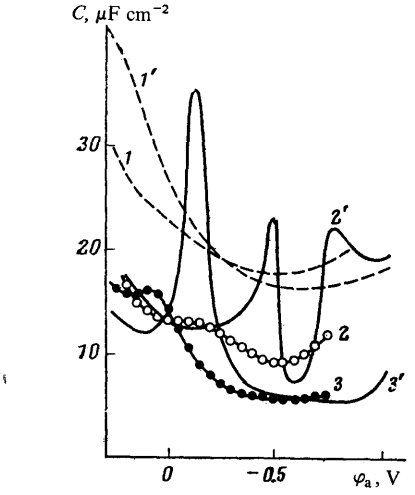


Figure 3. Differential capacitance curves for bismuth (curves *1–3*) and mercury (curves *1′–3′*) in 1 *N* potassium sulphate (bismuth) and sodium sulphate (mercury) solutions with added coumarin; coumarin concentration (M): 1) and 1′) 0; 2) and 2′) 7×10^{-4}; 3) and 3′) 5×10^{-3} (the electrode potentials were measured relative to the zero-charge point.

The difference between the adsorption behaviour of organic compounds on mercury and bismuth becomes appreciably enhanced for high positive surface charges. Experimental data have shown that anodic adsorption–desorption maxima for aliphatic compounds on bismuth are displaced by 0.1–0.15 V towards less positive values of φ than on mercury[27–29]. The main cause of this effect is the appreciable intensification of the chemisorption of water molecules with increase of ϵ on bismuth[46].

An important result of the different hydrophilic properties of metals and of different interactions of the functional group with the electrode surface in the adsorption of organic compounds is appreciable differences in the orientation of the adsorbate molecules in the adsorption layer[27–29,39–45]. On a bismuth electrode, organic compounds are oriented more vertically in the adsorption layer than on the mercury surface. The differences between the orientations of the adsorbed molecules are clearly shown in the adsorption of coumarin on bismuth and mercury. Coumarin molecules are adsorbed on mercury[47] and bismuth[48] in two different positions: in the vertical position at $\epsilon < 0$ and in an inclined position near $\varphi_{\epsilon=0}$. Fig. 3 shows that the regions corresponding to the adsorption of coumarin on mercury in the two positions are separated by narrow reorientation peaks; on the other hand, there is virtually no reorientation maximum on bismuth. Theoretical analysis of experimental $C-\varphi$ curves for the adsorption of coumarin, based on the model of three parallel condensers, showed that the orientation of coumarin molecules in the adsorption layer on bismuth is appreciably more vertical than on mercury, as a result

Although there are few literature data on the structure of the electrical double layer in non-aqueous solvents, nevertheless one might assert that the specific interaction of solvent molecules with the metal surface in the dense layer is manifested also in non-aqueous solvents.

Table 3.

Solvent	$\Delta\varphi^{Bi-Hg}_{\epsilon<0}$, V	$\Delta\varphi^{Bi-Hg}_{\epsilon=0}$, V	$\Delta\varphi^{Bi-Hg}_{\epsilon<0} - \Delta\varphi^{Bi-Hg}_{\epsilon=0}$, V	Electrolyte
Water	−0.145	−0.190	−0.045	0.1 *N* Na_2SO_4
Methanol	−0.14	−0.18	−0.04	0.1 *M* NH_4F
Acetonitrile	−0.13	−0.16	−0.03	0.1 *M* $NaClO_4$
Dimethyl-formamide	−0.14	−0.25	−0.11	0.1 *M* $NaClO_4$
Dimethyl sulphoxide	−0.09	−0.15	−0.06	0.1 *M* $LiClO_4$

Table 3 presents the differences between the zero-charge potentials on mercury and bismuth ($\Delta\varphi^{Bi-Hg}_{\epsilon=0}$) and the potential differences at a constant high negative charge ($\Delta\varphi^{Bi-Hg}_{\epsilon=0}$) for various non-aqueous solvents[19]. The latter differences should depend relatively little on the nature of the solvent[34,49].

The data in Table 3 show that the values of $\Delta\varphi^{Bi\text{-}Hg}_{\epsilon \ll 0}$ (for $\epsilon = -10 - -17 \mu C\ cm^{-2}$) depend comparatively little on the nature of the solvent, while the dependence of $\Delta\varphi^{Bi\text{-}Hg}_{\epsilon = 0}$ is appreciably greater. Evidently in all the solvents investigated the preferential orientation of the dipoles with the negative ends towards the metal surface at $\epsilon = 0$ is somewhat more pronounced on bismuth than on mercury. Particularly notable effects are observed in dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). Comparison of the $\epsilon - \varphi$ curves for mercury and gallium or an indium–gallium alloy showed that near $\varphi_{\epsilon=0}$ for gallium or an indium–gallium alloy DMSO molecules are clearly oriented with the negative end of the dipole towards the electrode surface[49]. On the other hand, in acetonitrile the specific interaction between the acetonitrile dipoles and gallium or an indium-gallium alloy is extremely weak.

Table 4. The adsorption equilibrium constants.

Solvent / ion	H_2O	CH_3OH	C_2H_5OH	DMF	Acetonitrile
Na^+	−9	—	—	—	—
K^+	−7	−2.6	−5.0	—	—
NH_4^+	−6.7	—	—	−17.5	—
Rb^+	−3.8	−2.1	—	−14.3	—
Cs^+	−1.4	−1.6	—	−11.5	—
Cl^-	1.75	4	4.5	11.6	—
Br^-	4.5	6.1	—	12.5	11.1
I^-	8.1	10.4	11.7	14.0	14.7
I^- on (111) face	8.8	—	—	—	—
SCN^-	5.2	5.3	5.9	6.4	5.6
NO_3^-	0.4	—	—	3.2	—

The nature of the solvent has an appreciable influence on the adsorption of ions on electrodes. The most systematic data for the adsorption of ions from non-aqueous solvents are available for the bismuth electrode[17,19,50–56]. Table 4 presents the adsorption equilibrium constants ($\ln\beta_{\epsilon=0}$), referring to the virial isotherm, for various ions on bismuth.

Evidently the free energy of adsorption depends very strongly on the nature of the surface-active ion, and increases greatly on passing from cations to anions. Among alkali metal cations, Cs^+ and Rb^+ exhibit the highest surface activity, while the remaining cations are adsorbed much more weakly.

The significant difference between the free energies of adsorption of cations and anions shows that different types of forces are responsible for the specific adsorption of the two types of species. For a given ion, the free energy of adsorption depends significantly on the nature of the solvent. In the adsorption of cations from protic solvents (water and alcohols) the values of $\ln\beta_{\epsilon=0}$ are higher by several orders of magnitude than for adsorption from aprotic solvents (DMF). The main cause of this effect is the appreciable enhancement of the solvation of cations on passing to aprotic solvents[57]; the different energies of interaction of the corresponding solvent molecules with the electrode surface also play a definite role. The opposite phenomenon occurs in anion-active systems—the free energy of adsorption increases appreciably (with the exception of the SCN^- anion) on passing from protic to aprotic solvents, which is mainly associated with the weakening of the solvation of anions in aprotic solvents[57]. As a result of the weakening of the solvation of halides, in the series $I^- > Br^- > Cl^-$, aprotic solvents lead to the equalisation of the free energies of adsorption.

Judging from the available literature data[53], the free energy of adsorption of cations depends little on the nature of the electrode. On the other hand, the free energy of adsorption of anions on bismuth in aqueous and alcoholic solutions is appreciably lower than on mercury. In DMF (there are no data for mercury in acetonitrile) the energy of adsorption of anions on bismuth[56] is virtually the same as on mercury[58].

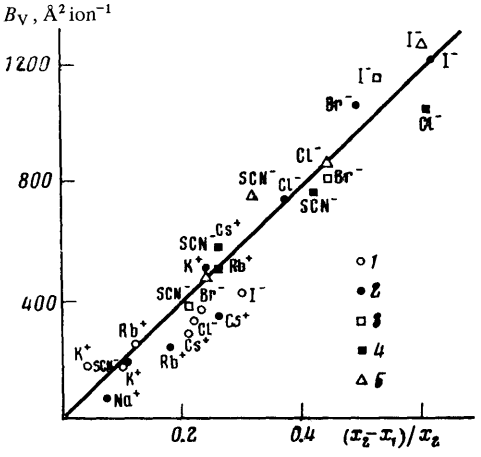


Figure 4. Variation of the second virial coefficient with the ratio $(x_2 - x_1)/x_2$ for different ions in different solvents: 1) water; 2) methanol; 3) acetonitrile; 4) dimethylformamide; 5) ethanol.

The nature of the solvent has a significant influence on the repulsion interaction between specifically adsorbed ions. It has been established for the bismuth electrode that the repulsion interaction is enhanced for a given ϵ = const., both with increase of the radius of the ions and with increase of the dimensions of the molecules of the solvent. Fig. 4 compares the second virial coefficients B with the ratios $(x_2 - x_1)/x_2$†.[17,51] To a first approximation, the relation illustrated in Fig. 4 may be regarded as linear; it suggests that the repulsion interaction of the adsorbed ions increases almost in proportion to the distance of the plane containing the charge centres of the specifically adsorbed ions from the outer Helmholtz plane. This relation can be accounted for qualitatively by the weakening of the screening effect of the diffuse layer on the repulsion between the specifically adsorbed ions with increase of the distance $x_2 - x_1$.[17,51,58,59]

IV. THE INFLUENCE OF THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER ON THE KINETICS OF THE CATHODIC EVOLUTION OF HYDROGEN

Kinetic studies have shown that surface-fused solid electrodes are the most suitable objects for the quantitative study of electrode reactions, particularly the cathodic

† x_1 and x_2 are the distances of the inner and outer Helmholtz planes from the electrode surface respectively.

evolution of hydrogen. When the surface of the metal is fused in an inert atmosphere, a stable state of the surface layer of metal is achieved and the occurrence of certain side reactions (the incorporation of cations from an alkaline solution), which greatly hinder the study of the true kinetics of hydrogen evolution, is strongly inhibited on electrodes of this kind[60].

Owing to the relatively high hydrogen overvoltage and the negative potential $\varphi_\epsilon = 0$, metals such as bismuth, tin, lead, and cadmium are suitable for the investigation of the influence of the structure of the electrical double layer on the rate of evolution of hydrogen in the region of polarisations close to $\varphi_\epsilon = 0$, where double layer effects should be manifested most clearly. According to the equation proposed by Frumkin on the basis of the theory of the slow discharge of H_3O^+,

$$\eta = a + \frac{1-\alpha}{\alpha}\psi_1 - \frac{1-\alpha}{\alpha}\frac{RT}{F}\ln c_{H_3O^+} + \frac{RT}{\alpha F}\ln i, \qquad (1)$$

the overvoltage η for a constant composition of the solution is influenced not only by the change in current density i, but also by the change in the ψ_1 potential. In Eqn. (1) a is a constant, α the transfer coefficient, and F the Faraday.

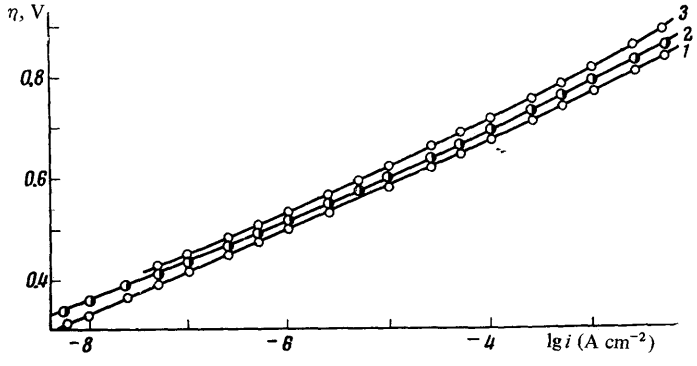


Figure 5. Polarisation curves for the evolution of hydrogen on bismuth in different solutions: 1) 1 N $HClO_4$; 2) 0.1 N $HClO_4$; 3) 0.1 N $HClO_4$ + 0.9 N $LiClO_4$.

Measurements on bismuth have shown that, in highly purified solutions (complete elimination of oxygen and of traces of other depolarisers), the variation of η with $\lg i$ in solutions of surface-inactive electrolytes is described by smooth curves without any sharp jumps in both aqueous[61,62] and methanol[63] media (Fig. 5). The low slopes of these curves, which depend on the acid concentration $c_{H_3O^+}$ and on η, are caused both by the change in the diffuseness of the double layer with electrode potential and electrolyte concentration and by the fact that the coefficient α for the hydrogen evolution reaction on bismuth exceeds 0.5.[61,62]

Using the values of ψ_0 instead of ψ_1 (this is justified to a first approximation for surface-inactive electrolytes), corrected Tafel relations (c.t.r.) were plotted for the hydrogen evolution reaction on bismuth. Such relations in 0.1 and 1.0 M $HClO_4$ solutions are linear over a wide range of potentials (Fig. 6). The results show that α is independent of acid concentration and amount to 0.61 ± 0.01. The higher value of the coefficient α was confirmed in a study of the dependence of η on $c_{H_3O^+}$ at a constant overall electrolyte concentration with the coefficient $(\partial\eta/\partial \ln c_{H_3O^+})_c = -36$ mV and also in the determination of the change in η caused by the increase of the overall electrolyte concentration $c_{H_3O^+}$ = const.

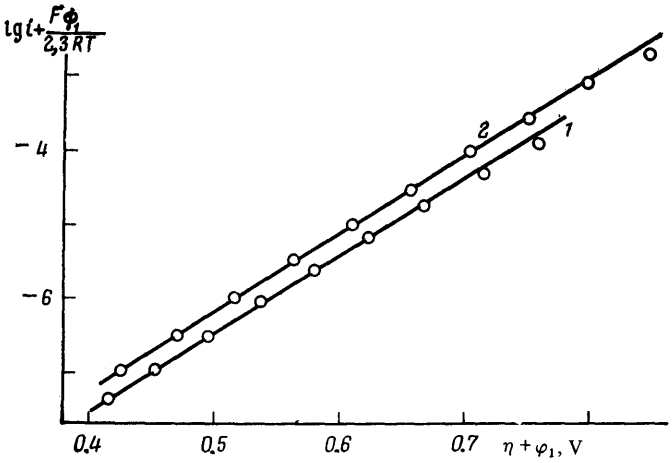


Figure 6. Corrected Tafel relations for the cathodic evolution of hydrogen on bismuth in $HClO_4$ solutions (N): 1) 1.0; 2) 0.1.

It has been shown[64] that, when the fundamental postulates of the diffuse layer theory and the double layer model proposed by Gram in the absence of specific adsorption are used, the slope of the η–$\lg i$ curve can be calculated from the formula

$$b_{theor} = \left[\frac{\alpha F}{RT} + \frac{2(1-\alpha)C_G}{\sqrt{4A^2c + \varepsilon^2} + \frac{2RT}{F}C_G}\right]^{-1}, \qquad (2)$$

where C_G is the capacitance of the dense layer and $A = \sqrt{DRT/2\pi}$ (D is the dielectric constant). Comparison of the experimental coefficients b with b_{theor} in 0.1 M $HClO_4$ solutions corresponding to different values of η for bismuth shows that, when $\eta < 0.8$ V, the agreement between experiment and calculation is extremely satisfactory. The significant discrepancies between the values of b for $\eta \geq 0.8$ V are probably caused by the specific properties of bismuth (metallisation) and are not related to the inaccuracy of Eqn. (2).[64]

Quantitative analysis of kinetic and capacitance data in terms of the model ideas developed by Krishtalik[65] showed that in the case of bismuth a fraction of the overall potential jump at the interface corresponds to the metallic phase[66]. It has been suggested that the decrease of α for $\eta \geq 0.8$ V ($\epsilon \gg 0$) is due to the metallisation of bismuth[29]. This hypothesis has been confirmed in a study of the chemisorption of water on bismuth[67].

Data similar to those quoted above were also obtained in a study of the kinetics of the evolution of hydrogen in the region of $\varphi_\epsilon = 0$ on gallium, indium, and their amalgams at elevated temperatures[68-71]. On the other hand, at room temperature the slope of the η – $\lg i$ curves for gallium[72], tin[73], and cadmium[14] proved to be virtually

independent of η, although the values of $\varphi_{\epsilon=0}$ for these metals are in the range of i accessible to measurement. The causes of such phenomena on cadmium and tin have not been established; they are probably associated with the enhanced hydrophilic properties of these metals[14,72].

Direct study of the kinetics of the cathodic evolution of hydrogen in an alkaline medium is possible on electrodes smoothed by surface fusion, because there is virtually no incorporation of alkali and alkaline earth metals into such electrodes owing to the comparatively overvoltage for such incorporation[60]. It has been found that the evolution of hydrogen on antimony[12,74], tin[75], and cadmium[14] electrodes takes place in alkaline solutions of different compositions via the mechanism involving the slow discharge of protons derived from water molecules. This mechanism was proposed for the first time by Frumkin and coworkers[76] for the nickel electrode as early as 1939.

Alkali and alkaline earth metal cations in solution exhibit an accelerating effect on the rate of evolution of hydrogen, which in the case of tin increases in the series from Li^+ to Cs^+ and from Ca^{2+} to Ba^{2+}.[75] In interpreting this effect, use was made of the hypotheses of both the specific adsorption of cations and of the involvement in the discharge process of the water molecules in the hydration shells of the cations[75,77]. As regards the influence of cations on η in an alkaline medium, there is a similarity between tin on the one hand and antimony[12,74] and cadmium[14] and partly liquid gallium[78] and saturated indium amalgam[77,79] on the other. The evolution of hydrogen on pure mercury in alkaline solutions is known to proceed via a mechanism different from that described above[79,80].

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