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POTENTIALS OF ZERO CHARGE, INTERACTION OF METALS WITH WATER AND ADSORPTION OF ORGANIC SUBSTANCES—I. POTENTIALS OF ZERO CHARGE AND HYDROPHILICITY OF METALS

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Abstract—The most reliable values of the potentials[*] of zero charge for metals not adsorbing hydrogen are obtained from the position of the minimum on the differential capacity–potential curves. These data are confirmed by the scrape method and by electron photoemission measurements. However, as it was first found from the comparison of the behaviour of gallium and mercury, at the same potentials referred to *pz* the adsorption behaviour of various electrodes with respect to the simplest aliphatic surfactants—aliphatic alcohols—differs. This was explained by preferential water chemisorption at electrodes of the gallium type. The determination of the position on the differential capacity curve of the amyl alcohol desorption peak relative to *pzc* gives a semi-quantitative estimate of the hydrophilicity of various metals, increasing in the sequence Hg < Bi < Sn < Pb < Cd < In < Ga. The potential at which the differential capacity of the dense layer starts to increase with decreasing negative charge shifts to more negative values relative to *pzc* in a similar sequence. The obtained results are compared with Trasatti's data. The case of antimony requires further investigation.

At present we have at our disposal reliable *pzc* values for a number of metals. In this communication we shall confine our investigation only to metals which do not adsorb hydrogen, so that the *pzc* values can be considered as being those of the potentials of zero free charge[1]. A detailed analysis, carried out recently by one of the authors, the results of which will be published elsewhere (see also[2]), leads to the conclusion that for solid metals not adsorbing hydrogen the choice of the *pzc* values should be based primarily on data obtained from the differential capacity—potential dependence. If the potential of the differential capacity minimum, which can be determined by direct or indirect methods[†] remains constant when the concentration of dilute symmetrical electrolyte solutions (usually $10^{-2}\,M$ and less) varies, this potential is the *pzc*. For one and two electrolytes a correction is necessary for the asymmetry of the C, φ dependence (C—differential capacity, φ—electrode potential)[4]. The method is applicable also in the case of slight specific adsorbability of one of the electrolyte ions if the concentration dependence of the potential of the minimum can be extrapolated to infinite dilution. When using this method, one should make sure that the differential capacity minimum corresponds to the maximum thickness of the Gouy layer, rather than being due to a certain peculiarity of the dense layer structure, which fact, however, was often not taken into account in experimental investigations.

The criterion in this case should be at least an approximate validity of the theoretical dependence of the depth of the minimum on electrolyte concentration[5].[‡]

The reliability of the *pzc* values found by this method is confirmed by good agreement between the results of the investigations on silver single crystals carried out at the Institute of Electrochemistry in Moscow, the Institute of Physical Chemistry in Sofia and at the Electrolysis Laboratory at Bellevue. We shall not dwell on the experimental details of the method used as these are discussed in[7]. The recommended *pzc* values of solid metals not adsorbing hydrogen are listed in the first column of Table 1. A possible error for the metals listed lies within ±0·02 V, or even less, except for copper, in which case it may exceed these limits. The data on solid metals are supplemented by *pzc* values for liquid metals obtained by the same method, or by usual techniques (electrocapillary measurements, dropping electrode). For comparison, in the second column are given the values obtained by Eyring *et al.* by means of the scrape method[8], which, although they cannot

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[*] The potentials are referred to as *she*.

[†] Indirect methods for determination of the differential capacity minimum of the diffuse part of the double layer allow to cover higher concentrations than the direct methods[3].

[‡] We speak only of an approximate validity, since it is not quite clear whether within the limits of the diffuse layer the dielectric constant can be always equated with its bulk value[6].

Table 1

Metal	Recommended *pzc* values	Electrolyte	*Pzc* found by the scrape method[8]	*Pzc* found from electron photoemission[9, 10]*
Ag (single crystal with different faces)	−0·66[12] (corr.)	$10^{-2}\,N\,\mathrm{Na_2SO_4}$	−0·64	
Ag (polycrystalline)	−0·7[11]	$10^{-3}\,N\,\mathrm{Na_2SO_4}$		
Ag (111)	−0·46[12, 14]	$10^{-3}\,N\,\mathrm{KF}$		
Ag (100)	−0·61[13]	$5\cdot10^{-3}\,N\,\mathrm{NaF}$		
Ag (110)	−0·77[14]	$5\cdot10^{-3}\,N\,\mathrm{NaF}$		
Au (polycrystalline)	0·18[28]	$2\cdot10^{-3}\,N\,\mathrm{NaF}$	0·12 (pH = 7)†	
Au (110)	0·19[16]	$5\cdot10^{-3}\,N\,\mathrm{NaF}$		
Bi (solidified drop)	−0·39[17]	$2\cdot10^{-3}\,N\,\mathrm{KF}$	−0·34	−0·39 ($10^{-3}\,N\,\mathrm{KNO_3} + 10^{-2}\,N\,\mathrm{KF}$)
Bi (111)	−0·42[18]	$10^{-2}\,N\,\mathrm{KF}$		
Cd	−0·75[19]	$10^{-3}\,N\,\mathrm{NaF}$		−0·80 ($10^{-2}\,N\,\mathrm{KCl} + 10^{-3}\,N\,\mathrm{HCl}$)
Cu	0·09[20]	$10^{-3}\,N\,\mathrm{NaF}$		
Ga	−0·69[21, 38]	$\mathrm{HClO_4}$, HCl $c \to 0$	−0·63‡ (solid)	
Hg	−0·193[22]			−0·19 ($10^{-2}\,N\,\mathrm{KF}$)
In	−0·65[23]	$3\cdot10^{-3}\,N\,\mathrm{NaF}$	−0·65	−0·63 ($10^{-2}\,N\,\mathrm{NaCl} + 10^{-3}\,N\,\mathrm{HCl}$)
Pb	−0·56[24]	$10^{-3}\,N\,\mathrm{NaF}$		−0·60 ($10^{-3}\,N\,\mathrm{HCl} + 10^{-2}\,N\,\mathrm{NaCl}$)
Sb	−0·15[25]	$2\cdot10^{-3}\,N\,\mathrm{KClO_4}$	−0·11	
Sn§	−0·38[26]	$2\cdot10^{-3}\,N\,\mathrm{KClO_4}$	−0·43	
Tl	−0·71[27]	$10^{-3}\,N\,\mathrm{NaF}$		
Ga + In (16·7%)	−0·68[43]	$10^{-3}\,N\,\mathrm{HClO_4}$		
Hg + Tl (41·5%)	−0·65[29]	$N\,\mathrm{Na_2SO_4}$		
Hg + In (64·6%)	0·64[59]	$N\,\mathrm{Na_2SO_4}$		

* The *pzc* values are obtained from the crossing of two photoemission current *vs* potential curves of two solutions of different concentrations; the composition of the solution with the higher concentration is given in the Table. The values for Cd and Pb are probably somewhat too negative owing to small $\mathrm{Cl^-}$ adsorption.

† By a similar method ("self-cleaning electrode") Noninsky and Lazareva[15] obtained $(\varphi_{\varepsilon=0})_{\mathrm{Au}} = 0{\cdot}05$.

‡ The authors of [8] refer this *pzc* value to solid gallium. Since the scrape method was used at the temperature close to the melting point of gallium, it would be more correct, probably, to refer this value to the liquid metal. The *pzc* of solid gallium seems to be somewhat more negative[31].

§ The data on the *pzc* of tin were obtained in sulphate solutions as the $\mathrm{F^-}$ anion is specifically adsorbed on tin.

pretend to such a high degree of reliability, have been carefully analyzed by the authors from the viewpoint of possible error sources. As can be seen from Table 1, the data in the first and second columns lie very close. The third column gives the values found from the potential dependence of the electron emission from metal into diluted electrolyte solutions. In spite of a somewhat lesser accuracy, these data are of great importance, since, unlike data obtained by other methods, their theoretical basis is a quantum-mechanical treatment of the elementary act of emission.

In most cases the *pzc* values in the first column of Table 1 are close to those recommended by Trasatti[32], or coincide with them (silver is an exception). This fact is no wonder as Trasatti made wide use of the same experimental material.

The position of *pzc* determines to a large extent the electric double layer structure and hence the adsorption behaviour of a metal. As a first approximation, it could be assumed that the same potentials referred to *pzc* (*i.e.* the same potentials in the reduced or φ scale according to Antropov[33], or in the rational scale according to Grahame[34]), correspond to the same surface charges and to the same adsorption of neutral molecules of organic compounds[33]. This conclusion is also of practical value, because it allows to extend the results of adsorption measurements made on mercury to solid metals. However the increase in the number of metals for which sufficiently accurate *pzc*, differential capacity and adsorption measurements had been carried out made it necessary to introduce a significant correction into this conclusion. This became clear for the first time in the investigation of the behaviour of liquid gallium carried out by Polianovskaya, Grigoryev and Bagotskaya[35,36,38]. While the difference between the *pzc* of Hg and Ga is 0·50 V, the difference between the potentials of the same negative charge amounts only to 0·17–0·18 V if this charge is large enough[35]. This discrepancy is due to a marked increase in the gallium electrode capacity with decreasing negative charge. Unlike mercury, this increase is observed also in solutions without surface-active anions and does not depend on the solution pH within the range where the capacity measurements on Ga are still possible (no oxide film has been formed as yet)[36]. This change in capacity was accounted for by specific adsorption and change in the orientation of water molecules, which turn with their oxygen end towards the Ga surface when its negative charge decreases[35,36,38]. The specific adsorption (chemisorption) of water is due to the stronger, as compared to mercury, hydrophilic nature of gallium. Lesser adsorbability, as compared to mercury, of organic compounds, in particular of aliphatic alcohols on gallium[35,36], and the results of the comparison of the work functions and the *pzc* difference[37] agree with this conclusion. The idea of the re-orientation of water molecules with changing surface charge was used earlier to explain the phenomena at the mercury/solution interface (appearance of a hump on the C, φ curves[39,40], the theory of the double layer of Bockris, Devanathan and Müller[41]), but it was clear from the obtained data that the re-orientation of water molecules exerts a stronger influence on the gallium/solution interface than on that between mercury and solution.

It followed from the works on gallium that the adsorption behaviour of a metal is determined not only by its *pzc* value, but also by its hydrophilic properties. Later it was pointed out that judging by its behaviour as adsorbent of aliphatic alcohols, iron is still more hydrophilic than gallium[42] and the difference between In + Ga alloy and mercury is not so large as that between gallium and mercury[43].

The effect of the interaction of metals with water on their *pzc* was considered by Trasatti[32]. Trasatti, who made extensive use of available experimental material, correlated the changes in the work function upon a change in the metal nature with those of *pzc*. According to Trasatti, the discrepancies between these two series of quantities can be removed by taking into account different orientation degrees of water molecules at *pzc* α. The prehistory of this problem will be discussed in part III of this communication. The same methods were used in[32] for estimation of α as were employed in[35,36,38] for comparison of the hydrophilicity of gallium and mercury, but, taking into account the fact that the water molecules orientation is determined by the interaction of the metal surface with the negatively charged oxygen atom, when considering the dependence of α on the metal nature. Trasatti made use of the notion of the electronegativity of the metal x_{Me}. According to Trasatti

$$\alpha = (2{\cdot}10 - x_{\mathrm{Me}})/0{\cdot}6 \tag{1}$$

where x_{Me} is the effective electronegativity of the metal surface. The notion of electronegativity was introduced by Pauling [45], who treated it as a chemical property characterising individual atoms.* Extending this notion to the metal surface, Trasatti considered it necessary to refine Pauling's values of x_{Me} (Pauling gave the values only to the first decimal place) and for gold, copper and transition metals also to correct them on the basis of empirical relations between the work function and the electronegativity. Trasatti comes to the conclusion that

$$x_{\mathrm{Me}} = 0{\cdot}50\, W_{\mathrm{Me}} - 0{\cdot}29 \tag{2}$$

for *sp* metals, except Ga, Zn and Al, for which

$$x_{\mathrm{Me}} = 0{\cdot}50\, W_{\mathrm{Me}} - 0{\cdot}55, \tag{3}$$

where W_{Me} is the work function. In some cases, Trasatti suggests that instead of the experimental values of W_{Me}, "electrochemical work functions" should be intro-

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* The notion of electronegativity is treated differently by different authors[53,54].

Table 2

Metal	$\varphi_{\epsilon=0} - \varphi_d$	$-\epsilon_d$ Supporting electrolyte	$-\epsilon_d$ Supporting electrolyte + $C_5H_{11}OH$	Electrolyte
Ga[43]	0·32	13·0	8·0	0·1 N $NaClO_4$
In + Ga[43,44]	0·51	12·4	9·4	0·1 N Na_2SO_4
In[2,44]	0·51	13·2	9·2	0·1 N Na_2SO_4
Cd[48]	0·55	14·3	9·5	0·1 N KF
Pb[49]	0·67	12·8	9·4	0·1 N Na_2SO_4
Sn[50]	0·63	13·2	9·3	0·1 N Na_2SO_4
Bi[51]	0·70	12·6	9·0	0·1 N K_2SO_4
Hg[52]	0·74	13·3	9·3	0·1 N NaF

duced, *ie* the values which are in better agreement with the *pzc* and other electrochemical characteristics of the metal. This suggestion can be considered to be justified, if we take into account the greater reliability of the determination of *pzc* of a number of metals, than that of W_{Me}. According to Trasatti, $x_{Me} = 1{\cdot}5$ for all transition metals ($\alpha = 1$); for copper and gold $\alpha = 0$.

Trasatti's work is undoubtedly of great interest. In the case of cadmium he succeeded in predicting correctly its hydrophilic properties prior to the publication of the relevant experimental data. Unfortunately, the *pzc* values given by Trasatti for aluminium, zinc and transition metals do not satisfy the modern reliability requirements. Trasatti did not take into account the dependence of *pzc* on the crystal face orientation found for silver[12,14] and bismuth[18], and for polycrystalline silver he used an obviously incorrect *pzc* value −0·45[11]. These facts make some of his conclusions questionable.

In this communication we shall extend to a wider range of metals a criterion of the hydrophilicity already used in[43] in the comparison of the behaviour of gallium and the gallium–indium eutectic alloy, viz. the difference between the *pzc* and the cathodic desorption potential of the norm. amyl alcohol φ_d at a definite concentration of the surface inactive supporting electrolyte. Experimentally, the cathodic desorption potential is determined by the position of the peak on the differential capacity-potential curve. At sufficiently high adsorbate concentrations and attraction constant values in the Frumkin adsorption isotherm, the desorption peak potential corresponds to a half-coverage of the metal surface with adsorbate[46,47]. The first column of Table 2 lists the values of $\varphi_{\epsilon=0} - \varphi_d$ for 0·1 *M* norm. amyl alcohol solutions* and the second column— the corresponding values of the surface charge ϵ_d at φ_d in the absence and in the presence of surfactant, obtained by integration of the differential capacity curves.

The data on the dependence of the value of $\varphi_{\epsilon=0} - \varphi_d$ on the metal nature are illustrated in Fig. 1. The C, φ dependences of various metals used in compilation of Table 2 were obtained in different investigations with electrolytes of somewhat different ionic strength and containing various cations, which could have affected the position of the desorption peak.

From the determination of φ_d we obtain a very significant, but only qualitative assessment of the hydrophilicity, because the position of the desorption peak depends not only on the free energy gain upon substitution of water molecules by those of organic substance, but also on a number of other factors characterising the adsorbed layer (area/molecule, shift of *pzc*

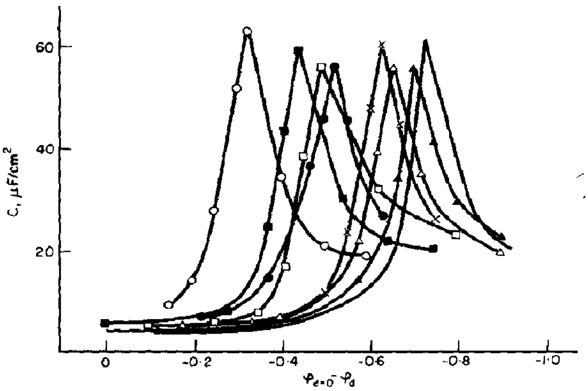

Fig. 1. Dependence on the potential of the differential capacity of 0·1 M norm. $C_5H_{11}OH$ solutions in the presence of 0·1 N surface-inactive electrolytes solutions (NaF, KF, Na_2SO_4 and $NaClO_4$). ○, Ga; ■, In + Ga; □, In; ●, Cd; ×, Sn; △, Pb; ▲, Bi; ———, Hg.

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* We did not include silver because some phenomena observed during amyl alcohol adsorption and desorption had not been cleared up[57], as well as zinc, for which *pzc* falls in the region of anodic metal dissolution and cannot be exactly determined. The choice of other metals included in Table 2 was determined by the presence of well-defined desorption peaks on the curves. Since the value of $\varphi_{\epsilon=0} - \varphi_d$ depends on the crystal face orientation, the values obtained on solid polycrystalline electrodes should be considered as being the result of averaging over the values referring to different faces. In the case of polycrystalline zinc, the desorption peak of tetrabutylammonium iodide splits into peaks characteristic of different single crystal faces[61].

upon surface coverage with organic substance, attraction constant value[46]). The finalization of these details requires further investigation. Moreover, the magnitude of the free energy gain itself depends not only on the free energy of wetting with water, but also on the interaction of the metal with the hydrocarbon chains of aliphatic compounds, primarily with the CH_3 groups, so that the results obtained are consistent with the term "hydrophilicity" rather in the sense used in colloid chemistry.* Judging from some data on adsorption from saturated hexyl alcohol solutions, in the sequence of metals in Table 2 antimony should be placed between Cd and Pb, close to Pb. According to Trasatti, the orientation degree of water at the surface of metals increases in the sequence Hg, Bi, Sb $<$ Pb, Sn $<$ Cd $<$ Ga. For Sb there is a discrepancy between his conclusions and ours, to which we shall return.

It is clear from Table 2, in spite of large differences in the value of $\varphi_{\epsilon=0} - \varphi_d$, that the values of ϵ_d (especially those referring to the supporting electrolyte), do not differ much.† The reasons for the dissimilar effect of the metal nature on these two quantities become clear when we consider the C,ϵ dependences of this group of metals. Figure 2 shows the dependences of the differential capacity of the dense layer C_s on the electrode charge (except curve 1, whose ordinates express the differential capacities C in N Na_2SO_4, not corrected for the diffuse layer capacities).‡ As is clear from this figure, at $\epsilon = \epsilon_d$ the capacities for different metals differ comparatively little.§ In other words, at the desorption potential of amyl alcohol, the differences in the hydrophilicity associated with those in the chemisorption and orientation of water molecules, smooth out significantly. From this point of view it would be interesting for comparison of the hydrophilicities to use a compound less readily desorbed than norm. amyl alcohol, such as tetrabutylammonium salts. Work in this direction has been started. The ϵ_d values given in Table 2 lie pretty close together. However, from what has been said concerning the factors, which can influence ϵ_d when the role of the metal hydrophilicity is excluded, follows that a certain dependence of ϵ_d on the metal nature can exist.

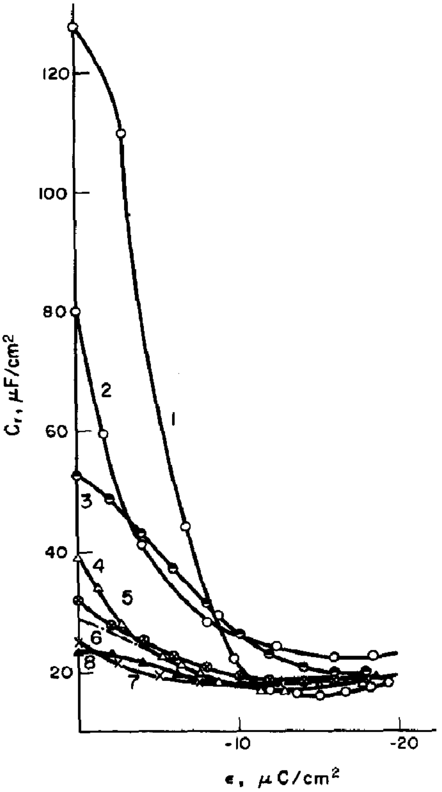

Fig. 2. Dependence on the potential of the differential capacity of the dense double layer: In [23]; Cd [55]; Sn [50]; Pb [24]; Hg [62]; Bi [61]; Sb [25]: Curve for Ga [35]—the differential capacity in N Na_2SO_4 not corrected for the diffuse layer capacity. Curves: 1—Ga [35]; 2—In [23]; 3—Cd [55]; 4—Sn [50]; 5—Pb [24]; 6—Hg [62]; 7—Bi [61]; 8—Sb [25].

The differences in the hydrophilicity observed at *pzc* depend on the surface charge value at which water chemisorption begins to manifest itself and on the rate of its further increase with the shift of ϵ towards less negative values.

While at sufficiently negative potentials the capacities for various metals (except indium) differ little from one another, at *pzc* a marked increase in the capacity is observed in the sequence Bi, Sb $<$ Hg $<$ Pb $<$ Sn $<$ Cd $<$ In $<$ Ga. This sequence almost coincides with the sequence in which, according to Table 2, the value of $\varphi_{\epsilon=0} - \varphi_d$ decreases (antimony is not included in Table 2, for Sb data on amyl alcohol adsorption are absent, but in this case there seems to be a discrepancy).‖

The quantitative relation between the capacity of the dense part of the electric double layer and the interaction of metal with water dipoles will be considered in part III of this communication.

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* Possibly, the adsorption value could be also used as a criterion of the hydrophilicity of a metal.

† The closeness of the ϵ_d values at the desorption potential of alcohols from mercury and gallium surface was first pointed out in[58].

‡ These should not differ much from C_s.

§ In comparing the differential capacities of various metals, In (and also In + Ga) should be treated separately, as in their case the capacity retains a higher value at the most negative ϵ than for other metals. The reason of this specific behaviour of indium is as yet not clear.

‖ This discrepancy, as well as the somewhat lower differential capacity value at *pzc* of Bi is possibly due to the semimetallic nature of Bi and Sb.

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