

HYDROPHILICITY SERIES OF WEAKLY HYDROGEN-ADSORBING METALS, AND THE POSITIONS OF THE GOLD AND SILVER ELECTRODES IN THIS SERIES

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A hydrophilicity series of weakly hydrogen-adsorbing metals was set up on the basis of available literature data for the differential capacity of the compact part of the electric double layer in aqueous solutions of inactive electrolytes at the zero-charge potential and for the potentials of the desorption peaks of $n\text{-C}_5\text{H}_{11}\text{OH}$ on the rational scale of 0.1 M solutions. It was shown that the metals can be arranged in the following sequence of increasing hydrophilicity: $\text{Tl}, (\text{Tl-Ga}) < \text{Hg} < \text{Bi}, \text{Sb} < \text{Pb} < \text{Sn} < \text{Cd} < \text{Au} < (110), \text{Au}(100), (\text{In-Ga}), \text{In} < \text{Ga}, \text{Ag}(100), \text{Ag}(111), \text{Ag}(110), \text{Zn}(0001), \text{Zn}(10\bar{1}0), \text{Zn}(11\bar{2}0)$.

It is of fundamental significance to set up a hydrophilicity series of metals, since the specific interaction of water molecules with electrode surfaces has great influence on electric double-layer structure and adsorption [1] and also on electrochemical reaction kinetics [2].

In a paper [3] dealing with double-layer structure on polycrystalline gold electrodes, the opinion was put forward that any increase in the free energy of water adsorption on electrodes should lead to a decrease in dielectric permittivity in the compact part of the electric double layer and to a corresponding decrease in differential capacity, C_H , of the compact part of the double layer. The C_H values found on Au, Hg, and Bi were compared in [3], and it was concluded that Au is the most hydrophobic metal, since the C_H values found on it near the point of zero charge are 2 to 3 $\mu\text{F}/\text{cm}^2$ higher than those on Hg, and those found on Hg similarly are higher than those on Bi. According to [3], this conclusion is supported by data for the adsorbabilities of halide ions on Au, which are substantially higher than those on Hg. A lower hydrophilicity of Au as compared to Hg was also concluded by Trasatti after an analysis of the relative values of zero-charge potentials and work functions of the metals, as well as on the basis of high adsorbability of halide ions on Au [4]. He assumed that the adsorption potential drop of water on Au is zero. Thus, the opinion that Au is the most hydrophobic metal is maintained to date in the international literature. Relying on the concepts developed by him, Trasatti concluded that the hydrophilicity of silver electrodes is close to that of mercury [4].

It had been shown already in [5], in a comparison of electric double-layer structure on Ga and Hg in solutions of inactive electrolytes, that the specific adsorption of water on an electrode gives rise to higher differential capacity of the compact part of the double layer. This is due to the additional expenditure of charge required to compensate the change occurring with electrode potential in the adsorption potential drop of water on account of reorientation of water dipoles in the surface layer. Thus, on liquid Ga in 1 N Na_2SO_4 one has $C = 135 \mu\text{F}/\text{cm}^2$ at the potential of zero charge, which is about 4.5 times higher than the value on Hg.*

A hydrophilicity series of weakly hydrogen-adsorbing metals set up on the basis of relative C_H values at $q = 0$ (q is the charge density of the electrode surface) had first been reported in [1]. The reported hydrophilicity sequence of the metals is in qualitative agreement with the positions of the desorption-peak potentials of $n\text{-C}_5\text{H}_{11}\text{OH}$ on the rational scale ($E_{\text{des. peak}} - E_{q=0}$) for the same metals [1]. Desorption of the organic compound should occur at the same potential drop in the compact part of the double layer on all metals, provided the negative desorption peak of the physically adsorbed organic compound occurs in the region of potential corresponding to high negative charge density where the state of water on the electrode surface no

* It is not possible to calculate the value of C_H on Ga, since the Gouy-Chapman theory does not work on this electrode [6]. However, the suggestion is justified that the C values measured in 1 N solution are close to C_H .

TABLE 1. Values of $C_H^{q=0}$ and $E_{\text{des.peak}} - E_{q=0}$ for Different Electrodes

Electrode	$C_H^{q=0}$, $\mu\text{F}/\text{cm}^2$	$E_{\text{des.peak}} - E_{q=0}$, V
Tl	24,5 [7]	—
Tl-Ga (0,02 at. % Tl) *	24,5 [8]	—
Hg	29,5	-0,76 [9]
Bi	28 [10]	-0,70 [11]
Sb	23 [12]	—
Pb	32 [13]	-0,67 [14]
Sn	40 [15]	-0,63 [16]
Au (110)	50+ [17]	—
Au (100)	65-70+ [18] †	—
Cd	52 [19]	-0,55 [20]
In-Ga (16,4 at. % In) *	60 [21]	-0,51 [22]
In	80 [23]	-0,51 [22]
Ga	135 [5]	-0,32 [22]
Ag (100)	100 [24]	—
Ag (100)	63 [25] ‡	—
Ag (100)	140-150+ [26]	-0,36 [26]
Ag (100)	120-130+ [26] ‡	—
Ag (111)	100 [24]	—
Ag (111)	63 [25] ‡	—
Ag (111)	120-130+ [26] ‡	—
Ag (110)	105 [24]	—
Zn (0001)	—	-0,44 [27]
Zn (1010)	—	-0,36 [27]
Zn (1120)	—	-0,29 [27]

* Tl and In in the systems Tl-Ga and In-Ga are surface-active components. This has the effect that Tl-Ga alloys (0.02 at. % of Tl) and eutectic In-Ga alloy (16.4 at. % of In) in their properties are similar to the thallium and indium electrodes, respectively.

† It had been pointed out in [18] that the reproducibility of capacity values measured on the (100) face of Au single crystals varied between 10 and 20%. Reliable quantitative data for the (111) face of Au single crystals are lacking in the literature. The differential-capacity values measured in [17] on the (111) face depended on ac frequency.

‡ The $C_H^{q=0}$ value reported was calculated from data measured in Na_2SO_4 solutions. Because of the complications arising when determining the zero-charge potential in the case of asymmetric electrolytes, the $C_H^{q=0}$ value calculated from data for Na_2SO_4 is less accurate than that for KF.

longer depends on the nature of the metal. It follows that the alcohol's desorption-peak potential on the rational scale should be less negative the higher the adsorption-potential drop of water in the point of zero charge and, therefore, the more hydrophilic the metal.*

In recent years, data obtained in quantitative studies of electric double-layer structure were published for a number of new metals, and also for the individual faces of single crystals. It was of interest, therefore, to examine the hydrophilicity series while allowing for these results. Values for differential capacity of the compact part of the double layer at the zero-charge potential, $C_H^{q=0}$, in aqueous solutions of $n\text{-C}_5\text{H}_{11}\text{OH}$ on the rational scale ($E_{\text{des.peak}} - E_{q=0}$) in 0.1 M solutions of the alcohol are reported in Table 1 ($E_{q=0}$ is the electrode's zero-charge potential in a solution of inactive electrolyte).

It was shown in [28] that on metals such as Au and Ag where the zero-charge potentials of the faces differ substantially while the C_H values at $q = 0$ are much higher than those at $q \ll 0$, the C_H values measured at identical potentials relative to a constant reference electrode are different for different faces. Hence at the potential E_{min} corresponding to the minimum on the C vs E curves in dilute solutions,† the C_H values

* We know that the adsorption of aliphatic alcohols on mercurylike metals basically is due to their being "squeezed out" from the bulk of the solution to the interface.

† According to [28], the average charge of polycrystalline electrodes at E_{min} can substantially differ from zero, so that E_{min} need not correspond to the electrode's zero-charge potential.

TABLE 2. Values of $C_H^{q=0}$ and f for Faces (100) and (111) of Silver*

Silver face	$C_H^{q=0}$ $\mu F/cm^2$	f	Silver face	$C_H^{q=0}$ $\mu F/cm^2$	f
(100)	140-150	1,04 [26]	(111)	120-130	1,07 [26]
	120-130	1,07 [26]		100	1,10 [24]
	100	1,15 [24]		63	1,39 [25]
	63	1,24 [25]			

* The f -values reported in the table were taken from the original papers.

found for the polycrystalline electrode are less sensitive to the faces forming the electrode surface than those found on the individual single-crystal faces at the zero-charge potential, and do not reflect the nature of the metal. The complications arising in the interpretation of C vs E relations found for polycrystalline silver and gold electrodes had already been pointed out in [24, 29]. It follows from [24, 29] that these complications are due to the fact that electrode surface heterogeneity has different effects on the dependences of C on electrolyte concentration in the solution and on surface charge. It seemed appropriate, therefore, to consider only values of $C_H^{q=0}$ for the individual single-crystal faces for Au and Ag in Table 1. Values of $C_H^{q=0}$ on individual single-crystal faces of Au and Ag marked "+" had not been given in the original papers [17, 18, 26] and were calculated by us from the data reported there using the intercept produced on the ordinate axis by plots of $1/C$ against $1/C_d$ (C_d is the capacity of the diffuse part of the double layer), and allowing for the roughness factor; the latter (f) was found from the slope of the straight-line plot of $1/C$ against $1/C_d$.

One can see from Table 1 that the $C_H^{q=0}$ values on the faces of Ag single crystals vary between 60 and $150 \mu F/cm^2$. On the polycrystalline Ag electrode, the C_H values at E_{min} are substantially lower, viz., 31^+ [3], 26^+ [31], and $25 \mu F/cm^2$ [32].* A similar dependence is found for Au. On the (110) face of the Au single crystal $C_H^{q=0} = 50 \mu F/cm^2$, and on the (100) face $C_H^{q=0} = 65$ to $70 \mu F/cm^2$, while C_H on the polycrystalline Au electrode at E_{min} has values of 32 [3] and 40 [33] $\mu F/cm^2$. According to the data of [29], $C = 31 \mu F/cm^2$ at $q = 0$ on polycrystalline Au in $1 N HClO_4$. It follows from the relative size of differential capacity of the compact part of the double layer on the individual single-crystal faces and on polycrystalline electrodes that any disturbance of the crystallographic uniformity of the faces should be attended by a decrease in capacity of the compact part of the double layer. A correlation actually is seen between the $C_H^{q=0}$ values for a given face and the f values (Table 2). An increase in roughness factor is accompanied by a decrease in the value of $C_H^{q=0}$. Maximum values of $C_H^{q=0}$ were found on the (100) and (111) face of Ag single crystals grown electrolytically in a Teflon capillary and not subjected to subsequent polishing [26].

Reliable data for double-layer structure on Zn close to the point of zero charge in solutions of inactive electrolytes are lacking, since the metal dissolves at these potentials. Hence, only the potentials of the negative desorption peak of $n-C_5H_{11}OH$ are reported for Zn in Table 1.

It follows from the data reported in Table 1 that the metals can be arranged in the following sequence of increasing hydrophilicity: Tl, (Tl-Ga) < Hg < Bi, Sb < Pb < Sn < Au (110), Au (100), (In-Ga), In < Ga, Ag (100), Ag (111), Ag (110), Zn (0001), Zn (10 $\bar{1}$ 0), Zn (11 $\bar{2}$ 0).

The most hydrophobic metals include Tl and Hg. It has been shown in [34] that lower $C_H^{q=0}$ values on Bi and Sb relative to Hg are due the semimetallic properties of Bi and Sb, which are most pronounced close to the zero-charge potential and at $q > 0$. Hence the position of Bi in the hydrophilicity series is best defined from the desorption-peak potential of $n-C_5H_{11}OH$. The higher hydrophilicity of Bi and Sb relative to Hg was confirmed recently by data for the reduction kinetics of anions of the type of BrO_3^- [2].

The most hydrophilic metals include Ga, Ag, and Zn. It is not possible to date to place these metals in the sequence of increasing hydrophilicity, since the differential-capacity values determined experimentally on single-crystal faces are not sufficiently accurate, owing to their crystallographic nonuniformity.

It follows from the data reported in [17, 18] that the roughness factors of the (110) and (100) face of Au single crystals were roughly 1.5 to 1.6, implying marked disturbance of their crystallographic uniformity. This means that the $C_H^{q=0}$ values reported in Table 1 ($50 \mu F/cm^2$ for the (110) face and 65 to $70 \mu F/cm^2$ for

* The C_H values for E_{min} on polycrystalline electrodes marked "+" also were calculated by us from data reported in the original papers using the intercept produced on the ordinate axis by straight-line plots of $1/C$ against $1/C_d$, with the assumption that $q = 0$ at E_{min} . Values of f reported in the original papers were used in the calculation.

the (100) face) must be regarded as low. It follows that the hydrophilicity of the (110) and (100) face of Au single crystals at any rate is no less pronounced than that of Cd, and is much higher than that of Hg, even though it is not possible to date to define the true position of Au in the hydrophilicity series. The high surface activity of halide anions on Au cannot be used as evidence for its hydrophobicity, since the adsorbability of these ions is determined, not only by the hydrophilicity of the electrode metal but also by their interaction free energy with the metal. The hydrophilicity of Ag, for instance, is much more pronounced than that of Hg, but Cl^- and Br^- ions (their adsorption has been studied quantitatively on silver electrodes [31, 35]) are much more adsorbed on Ag than on Hg.

It must be noted in conclusion that the above hydrophilicity series of the metals, which was set up on the basis of $\text{C}_{\text{H}}^{\text{Q}=0}$ values, is in qualitative agreement with data obtained in [2] for the effect of electrode metal on the reduction kinetics of anions of the type of BrO_3^- , where specifically adsorbed water molecules are involved in the elementary discharge act.

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