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The Surface Potential of Water at Metal-Solution Interfaces*

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Relative values of the surface potential of water at metal-aqueous solution interfaces at the potential of zero charge are derived by comparing experimental charge-potential curves for various metals. The principle of the method is presented and discussed. Absolute values for all the other metals are obtained by estimating the absolute value of the surface potential of water on Hg. Three independent routes are suggested. They are described and discussed. Experimental results are presented. The final estimate suggests that the surface potential of water on Hg is between 0.07 and 0.08 V, probably closer to 0.07 V. Water molecules are oriented with the oxygen atom facing the solid for all the metals investigated. A model is proposed to explain the metal-dependent orientation of water at the interface with electrodes at the potential of zero charge.

INTRODUCTION

The aim of this work is to give a quantitative estimate of the surface potential associated with oriented water molecules at uncharged metal-solution interfaces. Although this quantity is very important in theoretical electrochemistry, very few attempts[1–3] have been made to go into the quantitative aspects in the case of Hg electrodes, unlike in the case of the surface potential at the air/solution interface[4–10]. Since previous approaches suffer from conceptual inadequacies, a careful reexamination of the entire matter, relying also on new experimental results, is thought to be needed.

It will be shown that only values relative to a reference metal can be derived[11] experimentally. Therefore, in order to obtain absolute values, it is necessary to try to estimate the absolute value of the surface potential of water on the reference metal, which is obviously Hg. This will be the crucial point of this approach which, in the present form, can be applied only to sp-metals.

SURFACES AND INTERFACES

Particles in the surface region of a phase are subjected to net forces directed towards the interior of the phase. The resulting force along the surface is the well known surface tension. Unbalanced forces directed towards the interior are expected to be orienting and ordering in regard to particles at the surface. In case of a metallic phase[12–14] (Figure 1), the electron density

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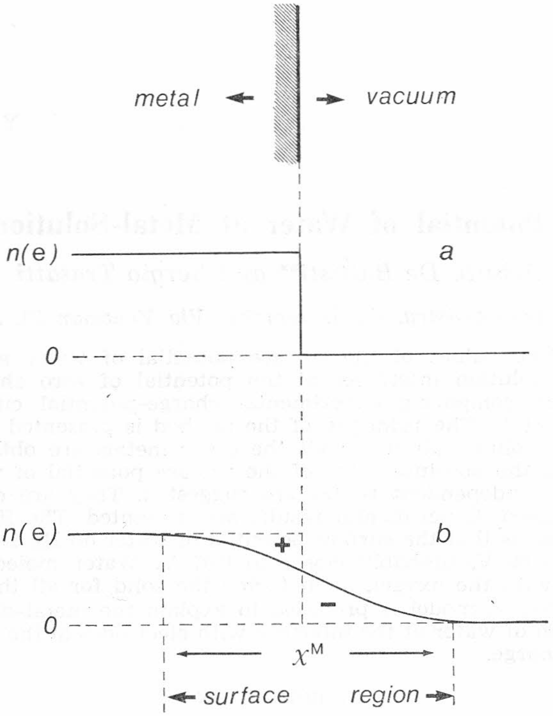

Figure 1. Origin of the surface potential on a metallic phase. (a) Ideal metal; (b) Real metal. n(e) is the electronic density in the solid.

at the surface should ideally change suddenly from the bulk value to zero. Under these circumstances, the work to extract an electron from the metal equals[15,16] the chemical potential of electrons:

$$W_{\text{extr}} = -\mu_e^M \tag{1}$$

However, on real metals the electron density goes smoothly to zero across the surface region, thus giving rise to the surface potential*, χ^M. The work to extract an electron from a real metal is the well known work function[12]:

$$W_{\text{extr}} = \Phi^M = -\mu_e^M + e\chi^M \tag{2}$$

which includes the surface contribution[14].

In the case of a liquid polar phase like water, a surface potential, χ^S, is expected[10] to arise as a result of preferential orientation of the dipoles at the surface due to unbalanced forces acting there.

As a metal is brought in contact with a liquid phase like water, and no charge transfer occurs between the phases, the interfacial region consists of the surface regions on the two phases. However, the surface potential on

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* By definition[15], χ is positive when the positive end of the dipole points to the phase.

the metallic phase, due to the presence of the liquid phase, may be not the same[7,17] as that at the free surface:

$$g^{\mathrm{M}}_{(\mathrm{S})}\ (\mathrm{dip}) = \chi^{\mathrm{M}} + \delta\chi^{\mathrm{M}}_{(\mathrm{S})} \tag{3}$$

and the surface potential of water due to the presence of the metal may not be the same as that at the free surface:

$$g^{\mathrm{S}}_{(\mathrm{M})}\ (\mathrm{dip}) = \chi^{\mathrm{S}} + \delta\chi^{\mathrm{S}}_{(\mathrm{M})} \tag{4}$$

$\delta\chi^{\mathrm{S}}_{(\mathrm{M})}$ and $\delta\chi^{\mathrm{M}}_{(\mathrm{S})}$ are interaction terms. Thus, the electrical potential drop across the interface is of a completely dipolar nature:

$$\Delta^{\mathrm{M}}_{\mathrm{S}}\varphi = g^{\mathrm{M}}_{\mathrm{S}}\ (\mathrm{dip}) \tag{5}$$

where*:

$$g^{\mathrm{M}}_{\mathrm{S}}\ (\mathrm{dip}) = g^{\mathrm{M}}_{(\mathrm{S})}\ (\mathrm{dip}) - g^{\mathrm{S}}_{(\mathrm{M})}\ (\mathrm{dip}) \tag{6}$$

If some charge transfer occurs, a term accounting for the presence of free charges must be introduced[15]:

$$\Delta^{\mathrm{M}}_{\mathrm{S}}\varphi = g^{\check{\mathrm{Z}}\check{\mathrm{S}}}_{.\mathrm{O}}(\mathrm{dip}) + g^{\mathrm{M}}_{\mathrm{S}}\,(\mathrm{ion}) \tag{7}$$

In this case, the dipolar term may be a function of the free charge.

DERIVATION OF THE RELATIVE VALUES OF THE SURFACE POTENTIAL OF WATER

Let us now consider a metal in contact with a liquid phase. Let E^{M} be the potential of metal M as measured against a reference electrode. The work to take an electron from the bulk of the metal to the bulk of the reference electrode through the external circuit must be equal to the work done through the internal circuit, that is through the liquid phase. Thus:

$$E^{\mathrm{M}} = \Phi^{\mathrm{M}}/\mathrm{e} + \delta\chi^{\mathrm{M}}_{(\mathrm{S})} - g^{\mathrm{S}}_{(\mathrm{M})}\ (\mathrm{dip}) + g^{\mathrm{M}}_{\mathrm{S}}\ (\mathrm{ion}) + \mathrm{const.} \tag{8}$$

where the constant term includes the energy barrier[16] at the solution-reference electrode interface.

Let us now consider the expressions of E for two metals:

$$E^{\mathrm{M}'} = \Phi^{\mathrm{M}'}/\mathrm{e} + \delta\chi^{\mathrm{M}'}_{(\mathrm{S})}(\mathrm{dip}) - g^{\mathrm{S}}_{(\mathrm{M}')}\ (\mathrm{dip}) + g^{\mathrm{M}'}_{\mathrm{S}}\ (\mathrm{ion}) + \mathrm{const.} \tag{9}$$

$$E^{\mathrm{M}''} = \Phi^{\mathrm{M}''}/\mathrm{e} + \delta\chi^{\mathrm{M}''}_{(\mathrm{S})}\ (\mathrm{dip}) - g^{\mathrm{S}}_{(\mathrm{M}'')}\ (\mathrm{dip}) + g^{\mathrm{M}''}_{\mathrm{S}}\ (\mathrm{ion}) + \mathrm{const.} \tag{10}$$

As the charge on the metal is zero, due to specific interactions the surface potential of the solvent on different metals may become different. As the charge is made negative, water molecules rotate and specific interactions tend to be compensated[18]. At the same strongly negative charge, the ionic term is the same by definition[15], while the dipolar term may also become metal-independent if the metal-solvent specific interactions can be neglected compared to purely electrostatic interactions. At strongly negative charges, the same double layer capacity, as measured with different metals[19], suggests that this may in fact be the case. If the interaction term $\delta\chi^{\mathrm{M}}_{(\mathrm{S})}$ is assumed to be the same for all metals[7], the difference in potential between two metals at

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* $g^{\mathrm{S}}_{(\mathrm{M})}$ (dip) is taken with the minus sign in that the orientation of the surface of the liquid phase is opposite to that of the solid phase.

the same strongly negative charge must equal the difference in work function. From eqs. (9) and (10):

$$\Delta^{M'}_{M''} E = \Delta^{M'}_{M''} \Phi/e \tag{11}$$

At the potential of zero charge chemical effects are present[17]. Thus, the difference in the potential of zero charge must equal the difference in work function *plus* the difference in the surface potential of the solvent (water):

$$\Delta^{M'}_{M''} E_{\sigma=0} = \Delta^{M'}_{M''} \Phi/e - \Delta^{M'}_{M''} g^{S} \text{ (dip)} \tag{12}$$

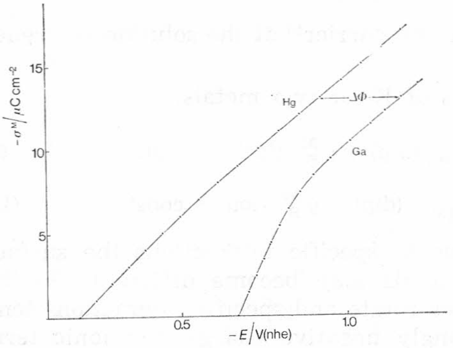
where subscript σ stands for charge on the metal. Therefore, if potentials are expressed in the rational scale[20], *i. e.* measured with respect to the potential of the zero charge of a given metal, the difference in the surface potential of water on the two metals in question:

$$\Delta^{M'}_{M''} E_{\text{pzc}} = \Delta^{M'}_{M''} g^{S} \text{ (dip)} \tag{13}$$

where:

$$E^{M}_{\text{pzc}} = E^{M} - E^{M}_{\sigma=0} \tag{14}$$

The above concepts can be best illustrated with the aid of experimental charge-potential curves which are easily obtained by the integration of double layer capacity curves. Figure 2 shows experimental charge-potential curves for Hg[21] in 0.1 M NaF and Ga[22] in 0.1 M $NaClO_4$. The two curves exhibit parallel linear portions where the orientation of water dipoles is thought to be metal-independent[18]. There, the difference in potential equals the difference in work function. If the two curves are now shifted to bring the potential to the rational scale as shown in Figure 3, the difference in potential at constant charge where the two curves are straight lines measures precisely the difference in the surface potential of water.



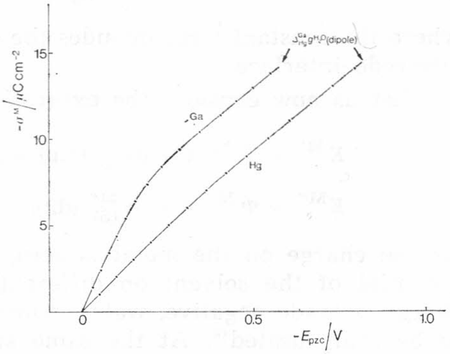


Figure 2. Experimental charge-potential curves for Hg in 0.1 M NaF solutions and Ga in 0.1 M $NaClO_4$ solutions. ΔΦ is the difference in work function.

Figure 3. The same curves as in Figure 2 plotted with potentials in the rational scale.

ESTIMATION OF THE SURFACE POTENTIAL OF WATER ON Hg

Relative values of the surface potential of water only can be obtained by using the above procedure. In order to obtain absolute values, the absolute value for at least one metal has to be estimated independently. As is obvious, Hg is the best reference metal, because with this metal reproducible and accurate measurements can be made. Therefore, the estimation of the surface potential of water on Hg appears to be the crucial point of the present approach.

The surface potential of a phase is not an experimentally measurable quantity[15]. However, to some extent, the interaction term $\delta \chi^{H_2O}_{(Hg)}$ can be obtained experimentally. Thus, three routes may be proposed to the estimation of the surface potential of water at the free surface. This quantity is slightly more easily accessible experimentally, although not straightforwardly. Furthermore, χ^{H_2O} has been more extensively investigated than $g^{H_2O}_{(Hg)}$ (dip). Thus, from eq. (4), the surface potential of water on Hg can be computed. The second route makes use of experimental potential shifts as measured upon adsorption of neutral organic substances on Hg, and the third route is a new suggestion in this field. Each separate approach will probably provide weak evidence for the estimated $g^{H_2O}_{(Hg)}$ (dip). However, since all the approaches lead to approximately the same value, it is thought that the reliability of the derived final estimate increases greatly.

First Route

According to the first route, the first step to be taken is the estimation of χ^{H_2O}. The only direct piece of evidence for the sign of χ^{H_2O} is the negative T coefficient as measured by Randles and Schiffrin[9]. This seems to suggest that χ^{H_2O} is probably positive, since the water layer should be increasingly disordered as the T is raised. The two sets of values for χ^{H_2O} in Table I have been suggested by other authors or derived from data in the literature. The first set refers to values for χ^{H_2O} as computed by subtracting[5,8] from the experimental[23] real free energy of hydration of the proton the ideal or chemical free energy of hydration of the proton as calculated on the basis of models[24]. In fact, by definition[15]:

$$\alpha^{0,H_2O}_{H^+} = \mu^{0,H_2O}_{H^+} + e\chi^{H_2O} \qquad (15)$$

Data in the literature[5] giving negative values for χ^{H_2O} have been rejected here because they are not in agreement with the sign predicted by the T coefficient.

The second set of data reports other experimental pieces of evidence in favour of a positive value for χ^{H_2O}. The first is the value suggested by Frumkin

TABLE I

Possible Values for the Surface Potential of Water at the Free Surface

χ^{H_2O} /V	Ref.
»a«	
0.13	24
0.1	5
0.04 ± 0.1	8
(—0.07 to 0.14)	
»b«	
0.1 to 0.2	4
0.142 (0.1 M CaCl)	25
0.13 (max)	9
0.08 (4 M NaCl)	28

et al.[4] about 20 years ago on the basis of a number of considerations. The second value is derived from the potential shift upon adsorption of benzene at the free surface of water[25]. It should be noted that when a neutral organic substance adsorbs at a surface, it replaces water molecules there[26] The change in potential drop across the surface depends on the dipole of water and the dipole of the organic substance[27]. If the latter is zero perpendicularly to the surface, then the potential shift may give a direct measure of the potential drop due to water dipoles. The third value was suggested as a possible maximum value by Randles and Schiffrin[9] from the experimental value of the T coefficient assuming a linear change of χ^{H_2O} with T. The last value is derived from adsorption potential shifts of unionized surfactants[28]. The value is lower than for the adsorption of benzene, presumably because the supporting electrolyte is much more concentrated. The allowance for the negative shift of χ^{H_2O} in the presence of anions[6,29] suggests that the derived value may be consistent with that obtained from the adsorption of benzene. From all of the above values, the final estimate is:

$$\chi^{H_2O} = 0.13 \pm 0.02 \text{ V} \tag{16}$$

corresponding to water molecules pointing on average their oxygen atoms towards the gas phase.

With regard to the interaction term $\delta \chi^{H_2O}_{(Hg)}$, its sign can be estimated from the difference in the T coefficient of the surface potential at the air-solution and Hg-solution interface, respectively, as measured by Randles *et al.*[9,30]. Judging from the higher value at the Hg-water interface[30] (—0.57 mV k^{-1}) than at the free water surface[9] (—0.4 mV k^{-1}), the above mentioned authors have suggested that the orientation of water may be higher at the former interface than at the latter. In fact, what Randles and Whiteley[30] measured was the T coefficient of the potential of zero charge of Hg. From eq. (8), with $g_S{}^M$ (ion) = 0 by definition at the potential of zero charge, the T coefficient of the potential of zero charge is given by:

$$\partial E_{\sigma=0} / \partial \mathrm{T} = \partial(\Phi^{M}/e) / \partial \mathrm{T} - \partial g^{H_2O}_{(Hg)}(\mathrm{dip}) / \partial \mathrm{T} \tag{17}$$

It consists of two terms; one is the T coefficient of the work function and the other one is the true T coefficient of the surface potential of water. There is evidence[17] that the former is positive and probably higher than 0.1 mV K^{-1}. If this is accepted, eq. (17) suggests that the true T coefficient of $g^{H_2O}_{(Hg)}$ (dip) is very likely to be lower than that of χ^{H_2O}. Accordingly, the two surface potential terms appear to be both positive and probably $\chi^{H_2O} > g^{H_2O}_{(Hg)}$ (dip).

Some experimental data support the above view. Jakuszewski *et al.*[31] have measured with an extrapolation procedure the difference in surface potential at the free surface between ethanol and water. They have obtained:

$$\chi^{EtOH} - \chi^{H_2O} = -0.42 \text{ V} \tag{18}$$

Rybalka *et al.*[32] measured the zero charge potential shift of an Hg electrode upon adsorption of ethanol. From eq. (8), if $\delta \chi^{(S)}_{M}$ is taken in a first approximation as independent from the nature of the adsorption layer, one can obtain:

$$\Delta^{EtOH}_{H_2O} E^{Hg}_{\sigma=0} = g^{H_2O}_{(Hg)}(\mathrm{dip}) - g^{EtOH(H_2O)}_{(Hg)}(\mathrm{dip}) = 0.36 \text{ V} \tag{19}$$

$g^{\mathrm{EtOH(H_2O)}}_{\mathrm{(Hg)}}$ (dip) indicates the surface potential due to a layer of ethanol molecules adsorbed at the interface with Hg from an aqueous solution. If the orientation of ethanol at full coverage can reasonably be assumed to be the same at the two interfaces, then $g^{\mathrm{EtOH(H_2O)}}_{\mathrm{(Hg)}}(\mathrm{dip}) = \chi^{\mathrm{EtOH}}$ and from eqs. (18) and (19):

$$\chi^{\mathrm{H_2O}} - g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}\,(\mathrm{dip}) = -\,\delta\chi^{\mathrm{H_2O}}_{\mathrm{(Hg)}} = 0.06\ \mathrm{V} \tag{20}$$

A similar estimation can be made from a set of results reported by Damaskin *et al.*[33] showing that the adsorption potential shifts for various alcohols at the Hg-aqueous solution interface differ by a constant amount from the adsorption potential shifts for the same alcohols at the air-solution interface. In this case:

$$(\chi^{\mathrm{ROH(H_2O)}} - \chi^{\mathrm{H_2O}}) - [g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}\,(\mathrm{dip}) - g^{\mathrm{ROH(H_2O)}}_{\mathrm{(Hg)}}\,(\mathrm{dip})] = 0.06\ \mathrm{V} \tag{21}$$

If the orientation of the organic molecules can reasonably be assumed to be the same at the two interfaces, the constant difference in eq. (21) can be attributed to the difference in water orientation at the two interfaces, *i. e.* to the interaction term $\delta\,\chi^{\mathrm{H_2O}}_{\mathrm{(Hg)}}$. Again, —0.06 V is obtained for this quantity.

As a conclusion of the first route to $g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}$ (dip), from the values for $\chi^{\mathrm{H_2O}}$ and the interaction term, a value of 0.07 V is obtained for the surface potential of water on Hg from eq. (4):

$$g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}\,(\mathrm{dip}) = \chi^{\mathrm{H_2O}} + \delta\chi^{\mathrm{H_2O}}_{\mathrm{(Hg)}} = 0.13 - 0.06 = 0.07\ \mathrm{V} \tag{22}$$

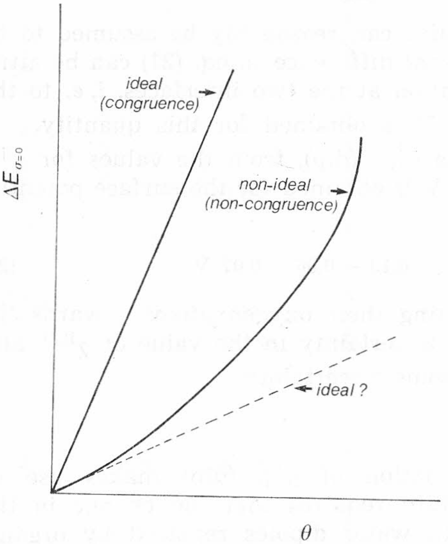
The sign implies water molecules pointing their oxygen atoms towards the metal. As shown in eq. (16), due to the uncertainty in the value of $\chi^{\mathrm{H_2O}}$, also the values of $g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}$ (dip) is affected by some uncertainty.

Second Route

The second approach to the estimation of $g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}$ (dip) makes use of adsorption potential shifts. This procedure requires that the change in the potential of Hg be only associated with water dipoles replaced by organic molecules. In fact, the organic molecule should not possess any finite dipole perpendicular to the surface. Two patterns of adsorption potential shift are known[34,35] (Figure 4). When the shift is linear with coverage, *ideal* substitution of dipoles occurs. This corresponds to the congruence of adsorption iso therms with respects to charge[36,37]. Congruence means that the parameters of the isotherm and therefore the mode of adsorption do not change with the electrical field across the interface. Accordingly, the shift is non-linear if the isotherms are not congruent. This corresponds to the *non-ideal* substitution of dipoles. However, under certain circumstances, at low coverages a limiting ideal substitution of dipoles may be observed. In this case parameters other than the adsorption potential shift are needed to decide.

The case of *n*-butanol is certainly non-ideal[34]. There is, however, some evidence[38] that at low coverages the orientation of the molecule may be flat with no dipole perpendicular to the surface. Müller suggested that the limiting slope of the potential shifts at the potential of zero charge should give $g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}$ (dip). Müller's results show that on average $g^{\mathrm{H_2O}}_{\mathrm{(Hg)}}$ (dip) may be about 0.07 V at $\sigma^{\mathrm{M}} = 0$. The evidence is weak, but this is only a first attempt.

The case of ethylene glycol[39] appears to be much better. On the whole bifunctional molecules are neutral and small molecules are rigid. As a result, ethylene glycol gives *ideal* adsorption potential shifts, as shown in Figure 5. The dashed line refers to the adsorption potential shift as measured from electrocapillary curves. The slope gives about 0.08 V for the surface potential of water. However, measurements have been remade using the streaming electrode technique[40] which does not suffer from capillary troubles[41]. The results in Figure 5. show that now the value of $g^{\mathrm{H_2O}}_{(\mathrm{Hg})}$ (dip) is about 0.07 V. With iodide ions in the supporting electrolyte the two sets of data coincide. In fact, in the presence of specific adsorption, capillary troubles tend to disappear[42]. It is interesting to note that in the latter case the orientation of water is apparently significantly reduced.



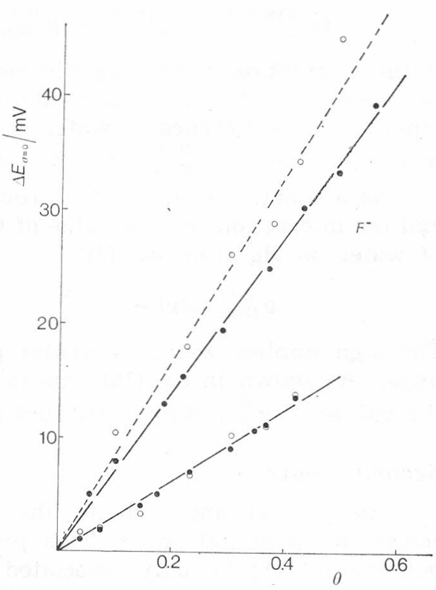
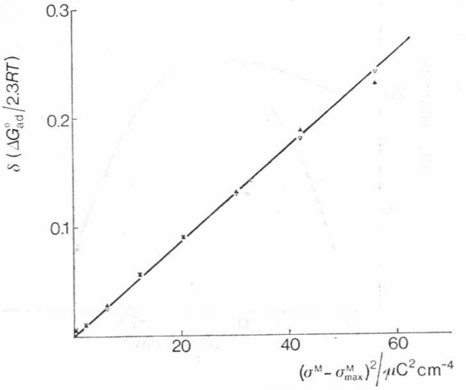


Figure 4. Sketch of possible patterns for the potential shift of an electrode upon adsorption of an organic substance.

Figure 5. Zero charge potential shift of a Hg electrode upon adsorption of ethylene glycol from aqueous solutions of different electrolytes. (○) Potentials of electrocapillary maximum. (●) Potentials as measured by the streaming electrode technique.

Ideality in the adsorption of ethylene glycol is emphasized by the quadratic dependence of the free energy of adsorption at zero coverage on charge[43]. Practically, adsorption exhibits a maximum at about $\sigma^{\mathrm{M}} = -3.5\ \mu\mathrm{C\ cm^{-2}}$. Figure 6 shows that the change in $\Delta G^{\mathrm{o}}_{\mathrm{ad}}$ from its maximum value is strictly a quadratic function of the change in charge from its value at the maximum. A very good parabola results for the change in $\Delta G^{\mathrm{o}}_{\mathrm{ad}}$ with charge and since the molecule of ethylene glycol adsorbs flat on the surface with no permanent dipole perpendicular to the surface, its behaviour is only due to induced dipoles, so that the interaction energy with the field in the double layer depends quadratically on the field.



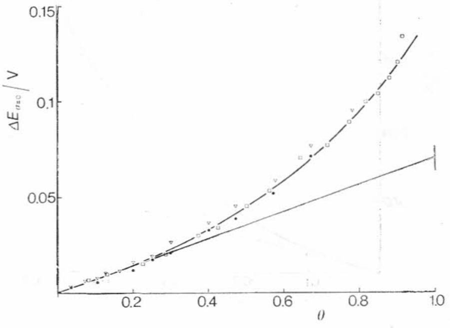


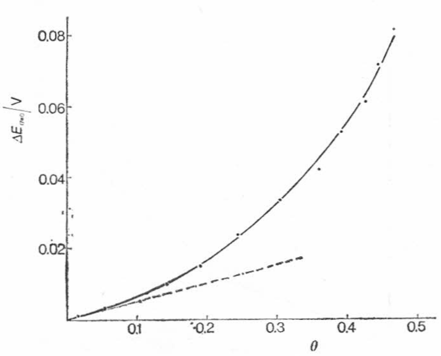
Figure 6. Change in free energy for adsorption of ethylene glycol on Hg as a function of the charge on the metal.

Figure 7. Zero charge potential shift of Hg upon adsorption of butane-1,4-diol. The limiting slope is also shown.

In the hope of obtaining equally good results and some support for the hypothesis put forward, butane-1,4-diol, whose structure was reasonably thought to be as favourable as that of ethylene glycol, was also investigated. This molecule was, in fact, studied by Garnish and Parsons[34,44], however, they made only electrocapillary measurements. Adsorption potential shifts measured with the streaming electrode technique are expected to be free from capillary troubles. Figure 7 shows the data of $\Delta E_{\sigma=0}$ plotted as a function of coverage as calculated from the isotherm given by Garnish and Parsons. Surprisingly, the behaviour is apparently non-ideal. Work is in progress to elucidate this point further. Probably the chain is not as rigid as in the case of ethylene glycol. However, at low coverages the charge for maximum adsorption is the same as for ethylene glycol and the free energy of adsorption is apparently a quadratic function of charge. Therefore, the limiting slope should refer to ideal conditions of dipole substitution. As shown in Figure 7 the limiting slope gives again a value of about 0.07 V.

The behaviour of nitriles is especially interesting[45,46]. They exhibit ideal behaviour at negative charges and non-ideal behaviour at positive charges. The charge for maximum adsorption is at —3.5 μC cm^{-2}, as for glycols. However, Figure 8 shows that the limiting slope of the shift in the potential of zero charge upon adsorption of acetonitrile is only about 0.04 V. The non-ideal behaviour of acetonitrile at positive charges is emphasized by the dependence of the free energy of adsorption upon charge (Figure 9). The favourable value of $\Delta G^{\circ}_{\mathrm{ad}}$ at positive charges is a result of the interaction of electrons in the triple bond of the CN group with the metal. At the potential of zero charge the behaviour is non-ideal even at low coverages and the limiting slope does not give $g^{\mathrm{H_2O}}_{(\mathrm{Hg})}$ (dip).

A particularly interesting case is that of succinonitrile. As shown in Figure 10 adsorption potential shifts exhibit ideal behaviour at all charges. However, the slope at the potential of zero charge gives 0.12 V for unity coverage. It is important to stress that the free energy of adsorption changes



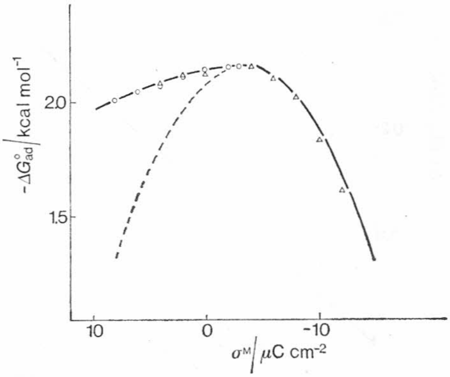


Figure 8. Zero charge potential shift of Hg upon adsorption of acetonitrile. The limiting slope is also indicated.

Figure 9. Relationship between the free energy of adsorption of acetonitrile on Hg and the charge on the metal.

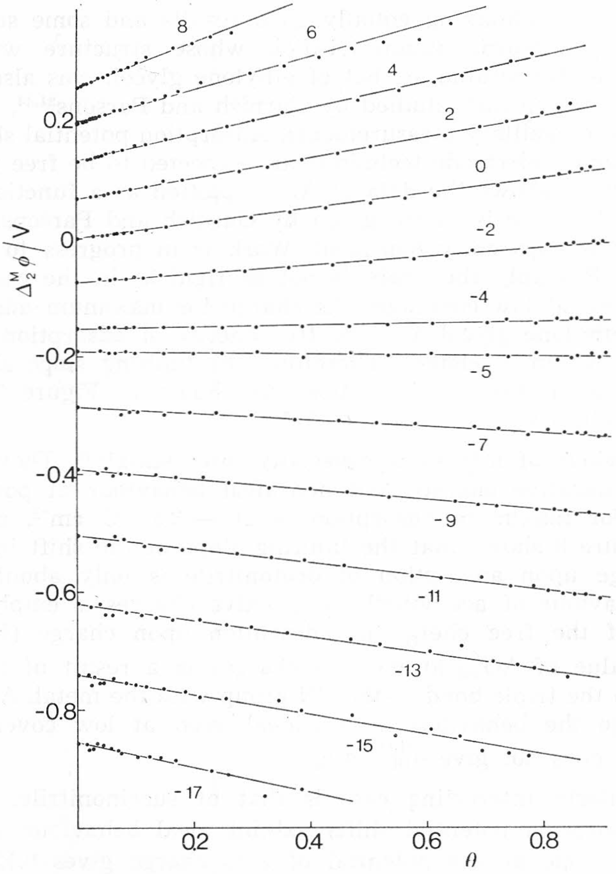
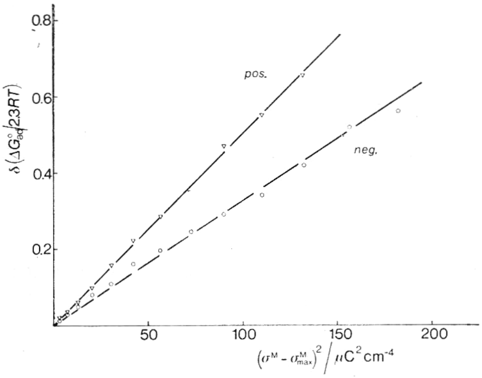


Figure 10. Shifts in potential at constant charge of a Hg electrode upon adsorption of succinonitrile.

quadratically with charge but with different dependences (Figure 11) at positive and negative charges, respectively, with respect to the charge of maximum adsorption, which is now at — 4.6 μC cm^{-2} more negative than for the other substances investigated. The explanation is in terms of a permanent dipole perpendicular to the surface with the positive end towards the metal, which does not reorient with the field. This dipole changes the polarizability of the molecule in opposite directions about a critical point close to the position of maximum adsorption. Detailed discussion of this view will be given elsewhere. What is relevant here is the attempt to correct the slope of the adsorption potential shift at $\sigma^M = 0$ by allowing for the presence of the fixed dipole, thus estimating the contribution due only to the substitution of oriented water dipoles.

The slope of the straight lines in Figure 10 is proportional to the slope of the relationship between ΔG° and charge at the same charge[47]. Figure 12 shows a plot of the slopes as a function of charge. The two straight lines intersect at — 4.6 μC cm^{-2} and their slopes are now proportional to the slopes of the straight lines in Figure 11 which are derived independently, and are in turn proportional to the polarizability[37] of the adsorbate molecule. According to the arguments given above a molecule of succinonitrile freed from the effect of the fixed dipole should exhibit a polarizability which is the mean of the two experimental polarizabilities, and a charge of maximum adsorption approximately equal to that of other nitriles. The line in Figure 12 has been drawn with a slope intermediate between the slopes of the two experimental straight lines and crossing the horizontal axis at — 3.5 μC cm^{-2}. It can be seen that the adsorption potential shift expected for such a molecule at $\sigma^M = 0$ is about 0.078 V, which practically coincides with the previous estimates



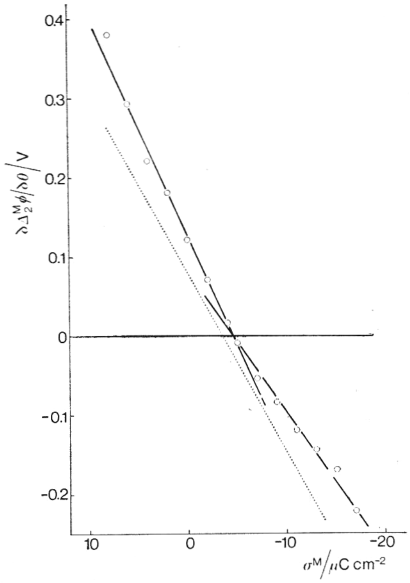


Figure 11. Change in free energy for the adsorption of succinonitrile on Hg as a function of the sign of the charge on the metal with respect to the charge of maximum adsorption.
Figure 12. The slopes of the plots in Figure 10 as a function of charge. (———) Calculated from the plots in Figure 11; (.....) After correction for the effect of the fixed dipole.

for $g^{H_2O}_{(Hg)}$ (dip). Figure 13 shows the experimental dependence of ΔG^o_{ad} upon charge and the theoretical dependence expected after allowance for effects due to the fixed dipole. The latter is thought to arise as a result of the two CN groups being slightly turned towards the solution.

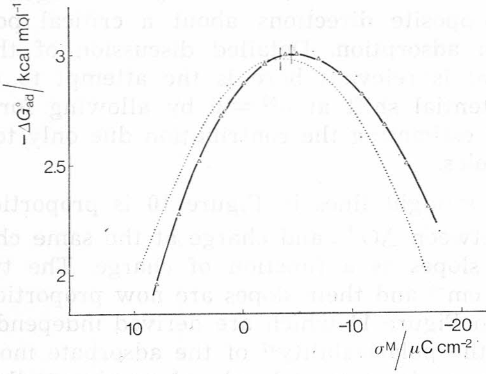


Figure 13. Relationship between ΔG^o_{ad} and the charge for the adsorption of succinonitrile on Hg. (△) Experimental results; (. . . . .) After correction for the effect of the fixed dipole.

Third Route

The third route to $g^{H_2O}_{(Hg)}$ (dip) is a new suggestion. It makes use of simple charge-potential curves from the integration of double layer capacity data in solutions with neither specifically adsorbable ions nor added organic substances. This procedure applies best to the range of negative charges. The change in the potential of an electrode as the charge is changed is usually split[48,49] into a dipole contribution and a free charge contribution:

$$\Delta_0^\sigma \, \Delta_S^M \varphi = g_S^M \text{ (ion)} + g^S \text{ (dip)} \tag{23}$$

The dipole contribution is due to the reorientation of water molecules under the action of the electric field, and the free charge contribution is governed by a capacity term which refers to the conditions of constant orientation of dipoles. Thus:

$$\Delta_0^\sigma \, \Delta_S^M \varphi = \sigma^M / K^i + g^S \text{ (dip)} \tag{24}$$

where K^i is practically the inner layer capacity at constant orientation of water dipoles, and:

$$g^S \text{ (dip)} = g^S_{(M)} \text{ (dip)} + g^S_{(\sigma)} \text{ (dip)} \tag{25}$$

Eq. (25) separates specific interactions from simply electrostatic interactions.

Figure 14 shows the charge-potential curve for the Hg-water interface derived by the integration of double layer capacity curves in fluoride solutions[21] after correction for diffuse layer effects. If the linear portion of the curve is assumed to involve constant orientation of dipoles, then the extrapolated straight line will intersect the potential axis at a point separating the dipole contribution from any other contribution. In Figure 14 segment ab measures

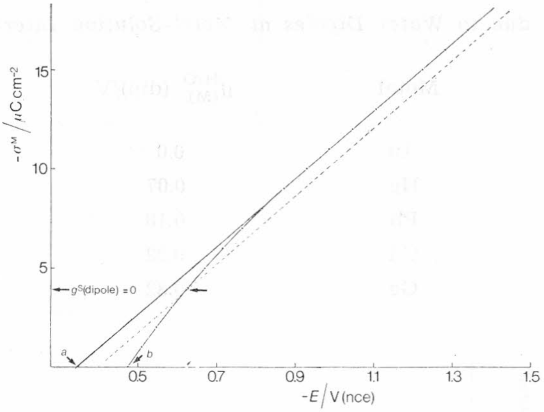


Figure 14. Charge-potential curve for Hg in 0.1 M NaF after correction for the diffuse layer effect. (———) See text.

the maximum dipole contribution from the potential of zero charge up to the most negative charges. This contribution is the sum of dipoles with the negative end towards the metal at $\sigma^M = 0$ and dipoles with the positive end towards the metal at the most negative charges. It is possible to demonstrate that a straight line parallel to the extrapolated line must cross the experimental curve at a point where the net dipole contribution (orientation) is zero if it starts from a potential where the orientation of water is zero. At this charge the configurational entropy of the double layer is expected to exhibit a maximum[50]. The results of Hills and Hsieh[51] show that a sharp maximum of entropy actually exists at $-4\ \mu C\ cm^{-2}$. Now, if the straight line referred to above is made to cross the experimental curve at $-4\ \mu C\ cm^{-2}$, the intercept on the potential axis represents the potential of zero charge of Hg freed from contributions due to preferentially oriented water dipoles. Thus, the distance between the intercept and the actual potential of zero charge gives the surface potential associated with water molecules at the potential of zero charge. $g^{H_2O}_{(Hg)}$ (dip) is shown from this approach to be about 0.075 V.

ABSOLUTE VALUES OF SURFACE POTENTIAL OF WATER. ROLE OF THE METAL

Absolute values for the surface potential of water can now be obtained. $g^{H_2O}_{(Hg)}$ (dip) from all of the above discussion is shown to be between 0.07 and 0.08 V, probably closer to 0.07 V. For the sake of simplification, it will be taken here as 0.07 V. In case of metals for which the experimental results are more clear-cut[7–17], eq. (13) gives for the surface potential of water, as summarized in Table II, values between 0 V and 0.32 V. These are positive surface potentials but negative contributions to the total potential drop across the double layer.

A correlation can be found between the surface potential of water and the nature of the metal. Water molecules interact with the metal surface essentially through the oxygen atom. The affinity of the metal for oxygen,

TABLE II

Surface Potential due to Water Dipoles at Metal-Solution Interfaces at the PZC

Metal	$g_{(M)}^{H_2O}$ (dip)/V
Au	0.0
Hg	0.07
Pb	0.18
Cd	0.22
Ga	0.32

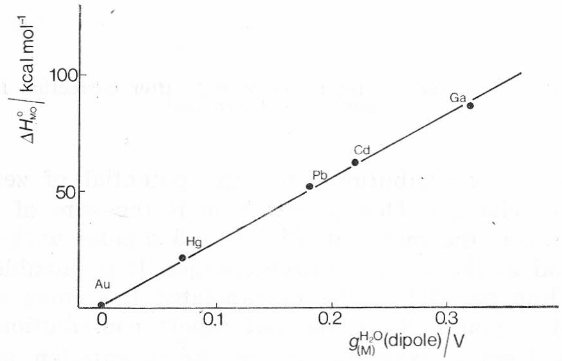


Figure 15. Correlation between the orientation of water at the interface with metals and the affinity of metals for oxygen expressed in terms of the enthalpy of oxide MO formation.

and hence for water, could be expressed to a first approximation in terms of the enthalpy of formation of the oxide MO:

$$\mathrm{M\,(s)} + 1/2\,\mathrm{O_2\,(g)} \rightarrow \mathrm{MO\,(s)} \qquad (26)$$

where (s) stands for solid and (g) for gas. Figure 15 shows that a strictly linear correlation exists between the orientation of water and the strength of metal-water chemical interactions. Figure 15 makes it possible for an explanation in chemical terms to be given for the values of $g_{(M)}^{H_2O}$ (dip) on the various metals.

COMPARISON WITH MODELS

Although the present approach is also based on a modellistic representation of the interface, values of $g_{(Hg)}^{H_2O}$ (dip) as derived here are essentially experimental values. Some comparison is possible with theoretical models. The first comparison regards the value of $g_{(M)}^{H_2O}$ (dip) at the potential of zero charge. As shown in Table III, the existing models[48,49,52], except for an earlier model by Bockris *et al.*[53], predict a residual orientation for water at the potential of zero charge with the oxygen atom towards the metal. The calculated values cover a somewhat wide range but on an average the order of magnitude predicted for $g_{(Hg)}^{H_2O}$ (dip) is close to the experimental value.

At the moment it is more difficult to comment on the difference in the dependence of the orientation on the free energy of water adsorption. Models[48,49] give an exponential dependence whereas the present approach ap-

TABLE III

Comparison with Predictions of Models

	Ref.	$g^{H_2O}_{(Hg)}$ (dip)/V
This work	—	0.07
Bockris *et al.* (1963)	53	0.0
Damaskin and Frumkin (1974)	48	0.05
Parsons (1975)	49	0.008
Bockris and Habib (1975)	52	0.03

parently suggests a linear dependence. Work is in progress to transfer results and suggestions ensued from this approach into a model for water at the interface with metals.

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SAŽETAK

Površinska napetost vode na granici faza metal-otopina

Achille De Battisti i Sergio Trasatti

Uspoređeni su eksperimentalni podaci o ovisnosti nabijenosti površine raznih metala o potencijalu, te su izvedene relativne vrijednosti za površinske potencijale vode na granici faza metal/vodena otopina na potencijalu kada je površina nenabijena. Opisan je i diskutiran princip metode određivanja tih relativnih vrijednosti. Procjenjena je apsolutna vrijednost površinskog potencijala vode za živu, a pomoću nje i odgovarajućih relativnih vrijednosti, određene su apsolutne vrijednosti površinskih potencijala za ostale ispitivane metale. Predložene su i diskutirane tri neovisne procedure. Na osnovu prikazanih eksperimentalnih rezultata procijenjeno je da je površinski potencijal vode na živi između 0.07 i 0.08 V. Spominje se da je orijentacija molekula vode za sve ispitivane metale karakterizirana atomom kisika u smjeru metalne površine. Predložen je model kojim se pokušava objasniti takova orijentacija vode na granici faza na potencijalu na kojem su elektrodne površine nenabijene.

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