CCA-1735

Progress in the Understanding of the Structure of the Metal Electrode/Solution Interface. Evolution of the Concept of Hydrophilicity*

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The metal-water interaction strength (»hydrophilicity«) plays a major role in determining both the structure of the interfacial region and the energetics of adsorption phenomena. A »hydrophilicity« scale can be established on the basis of a phenomenological approach for a series of sp-metals. It is shown that recent results for sd-metals (Cu, Ag, Au) cannot be organized in the same picture. This has lead to a reconsideration of the factors governing the behaviour of an electrode interface. The role of the surface electron gas, thus far underestimated, should be revaluated. This is what »physical models« emphasize as opposite to »molecular models« for which the response of the interface is simply that of a monolayer of solvent molecules. It is stressed that these conceptual developments do not clash with conclusions of the phenomenological approach based on the correlation of a few experimental parameters with some physicochemical properties of metals.

INTRODUCTION

The distribution of charged and neutral species at the electrode/solution interface is governed, together with the electric field, by a number of factors which can be expressed in terms of pairwise chemical interactions: particle-particle, particle-solvent, particle-metal and metal-solvent interactions.[1,2] Thus, specific adsorption is customarily described as arising from a competition between particle-solvent and particle-metal interactions.[3,4] Similarly, surface condensation can be understood in terms of competition between particle-particle and particle-solvent interactions.[5-8]

Although any similar description is only a first approximation (for instance, particle-solvent interactions are expected to differ in the bulk of the solution and at the interface, so that these interactions are anisotropic in the interfacial region),[1,9] the representation of the energetic situation in terms of separate single contributions is a great conceptual aid especially in double

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* Based on an invited lecture presented at the *7th »Ruđer Bošković« Institute's International Summer Conference on the Chemistry of Solid/Liquid Interfaces,* Red Island — Rovinj, Croatia, Yugoslavia, June 25—July 3, 1986.

layer modeling. In this respect, this paper is primarily devoted to discussing the implications of the correct description of the metal/solvent interaction.

2. PHENOMENOLOGICAL APPROACH TO HYDROPHILICITY

Several experimental parameters are expected to depend (among others) on the metal electrode/solvent interaction strength.[1,10] In view of the kind of interface, most of the parameters are electrical, e. g. the potential of zero charge, $E_{\sigma=0}$, and the differential capacitance, $C = d\sigma/dE$ where σ is the charge density on the metal surface. Other parameters are non-electrical in principle, in particular, the Gibbs energy of specific adsorption which is conceptually depicted as a solvent replacement reaction:[11]

$$S \text{ (ad)} + B \text{ (sln)} \rightleftarrows B \text{ (ad)} + S \text{ (sln)} \tag{1}$$
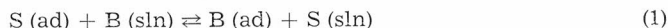
where S and B stand for solvent and adsorbing species, respectively.

In the particular (and most investigated) case of metal/water interfaces, the term »hydrophilicity«[12] is meant to indicate the »affinity« of the metal surface for water molecules.[13,14] This can be expressed (*i*) as a primary effect directly in terms of the metal/water interaction strength (which can be determined from gas phase adsorption) or indirectly in terms of the Gibbs energy of adsorption of species from the aqueous solution (which according to eqn. (1) includes the Gibbs energy of desorption of water molecules), or, (*ii*) as a secondary effect on such electrical parameters as $E_{\sigma=0}$ (which contain a contribution due to oriented dipole layers) and C (which depends on the permittivity of the interface, i. e. on how the dipoles at the interface are reoriented as the electric field is changed).

2.1. *The Potential of Zero Charge*

That different metals possess different potentials of zero charge was known long ago.[15] The difference was however attributed for long to the difference in the electronic energies at the Fermi level (i. e. the electron work function, Φ). An extended analysis of $E_{\sigma=0}$ vs Φ correlations has later revealed[16] that systematic deviations exist in fact. The deviations are related to the behaviour of the dipole layers at the interface and are thus expressed in terms of electrical parameters.

The relationship between $E_{\sigma=0}$ and Φ is the following:[1,16]

$$E_{\sigma=0} = \Phi + \delta\chi_0 - g \text{ (dip)}_0 + const \tag{2}$$

where $\delta\chi_0$ is the modification of the surface potential of the metal upon contact with the aqueous phase, and $g \text{ (dip)}_0$ is the contribution due to any preferentially oriented water dipole layer at the metal surface (which differs in principle and in practice from the surface potential at the water/vapour interface). Subscript »0« means that the parameters are those at $\sigma = 0$ and that they depend in principle on the state of charge of the interface.

The model from which eqn. (2) ensues (but the equation has a thermodynamic basis) is illustrated in Figure 1. The metal is depicted according to the »jellium« model[17] which consists of a uniform positive background (the positive charge of the ion cores smeared out uniformly) within which the valence electrons can move freely. When the latter impinge on the
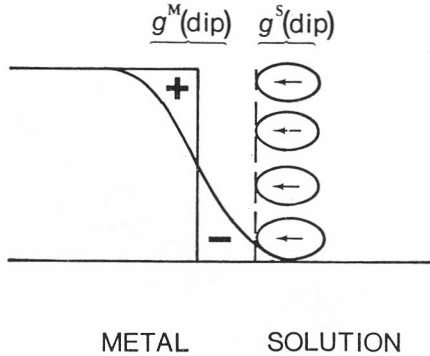
METAL   SOLUTION

Figure 1. Sketch of the metal/solution interfacial region to show the components of the potential drop as the charge on the metal is zero.

surface energy barrier, they are reflected back, but from an undefined point *inside* the barrier. This corresponds to free electrons protruding from the ion core edge thus giving rise to a surface dipole potential, χ.[18] As the metal is brought in contact with liquid water, the free electron surface distribution is disturbed by the eletron clouds of the approaching molecules. The effect is expressed by $\delta\chi$, while the orienting effect of the metal surface on the water molecules close to the solid wall is expressed by g (dip).

It is not possible to measure $\delta\chi_0$ and g (dip)$_0$ in eqn. (2) separately. Even the sum of the two is not accessible to experimental determination. Therefore, eqn. (2) can only provide information on the *relative* behaviour of different metals. The value of the »const« (which depends on the nature of the reference electrode only) is in fact unknown. Figure 2. shows a plot of $E_{\sigma=0}$ vs. Φ (both referred to Hg as the reference metal). Only sp-metals are included in the diagram, because for them the experimental parameters are most reliable.

Similar plots suffer from the drawback that the pair of experimental data for a given metal are usually obtained quite independently on different samples. Since both $E_{\sigma=0}$ and Φ are very sensitive to the state of the metal surface, the plot is unavoidably viziated by the lack of a perfect correspondence of the data to the same system.

Despite the above shortcomings, the plot in Figure 2 is most effective to obtain a quick and valid information on the state of metal/water interfaces. The figure shows that if the term

$$X = \delta\chi_0 - g \text{ (dip)}_0 \tag{3}$$

were metal independent, then all points would fall on a straight line of unit slope passing through the point of Hg. This is in fact not the case. All the points deviate from the straight line and it is intriguing that the deviations are always negative (the points fall on the left of the straight line). If we consider the form of eqn. (2), these deviations can be interpreted as due to a metal-dependent effect on the X term. Due to the lack of any experimental information on $\delta\chi_0$, the major part of the effect has been attributed[1,16] to g (dip)$_0$, i. e. to a different *orientation* of the water dipoles in contact with the metal surface.
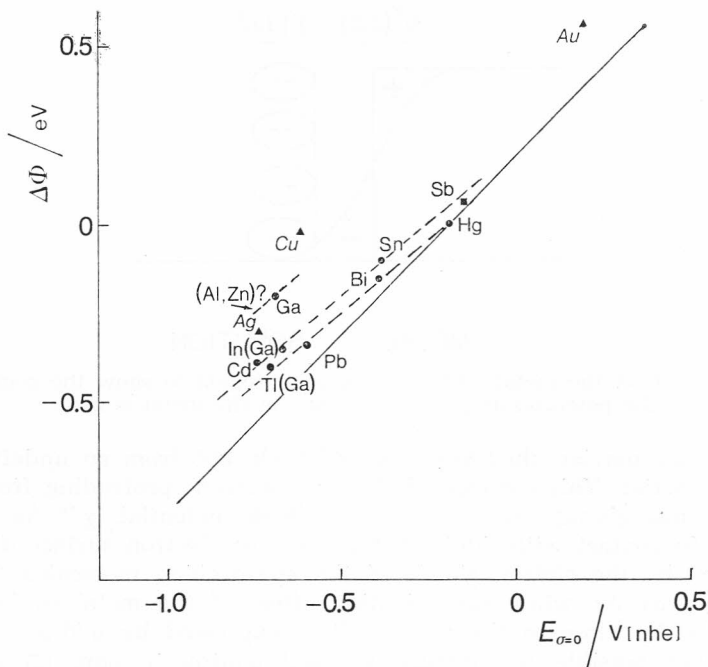
Figure 2. Plot of the electron work function (relative to that of Hg) vs the potential of zero charge. The data for Cu, Ag and Au are for the (110) face.

Finding a rationale behind the deviations in Figure 2 is a major task. It has been suggested[16] that all metals (except Ga) can be gathered in one group and since the deviations indicate that $E_{\sigma=0}$ becomes more negative than expected from the simple decrease of Φ along the series of metals, it has been concluded that this could be related to an increasing value of $g\,(dip)_0$, i. e. to a stronger preferential orientation of water with the oxygen atom towards the metal as Φ decreases. Thus, the »hydrophilicity« is here expressed indirectly by the electrical parameter $g\,(dip)_0$.

That water molecules interact with a metal surface through the oxygen atom is supported by independent pieces of evidence such as the descrease of Φ measured as water is adsorbed from the gas phase,[19,20] and quantum chemical calculations of water chemisorption.[21,22] Thus, the idea behind $g\,(dip)_0$ is that a higher value of this parameter corresponds to a more marked orientation of the molecular dipole as a consequence of a stronger metal-water interaction. Although this idea is supported by other kinds of correlations,[9,10,23,24] the picture is heavily based on neglecting the role of $\delta\chi_0$ which is in fact regarded as metal independent (though non-zero).[16]

One of the major consequence of the above approach is that a more negative value of $E_{\sigma=0}$ is expected for metals with a lower Φ, and a lower Φ should result in a stronger metal-water interaction. These aspects have been recently questioned starting from different positions. In one case,[25] it has been maintained that no general rule can be established since the points are rather scattered in the plot of Figure 2. However, this remark

stems from a not sufficiently selective analysis of the experimental data. It is in fact possible to distinguish more than one group, each including the sp-metals of one period of the Mendeleev table. The fact that Ga, Zn and probably Al belong to a different group was already suggested in an early paper by the present author.[16] It is not unreasonable from a *chemical* point of view that Cd, In and Sn, (and presumably Sb) and Hg, Tl, Pb, and Bi can form different groups. These are tentatively individuated in Figure 2. Whether the linear dependence of $E_{\sigma=0}$ on Φ run really parallel for the various groups is difficult to say, but they look like being so.

In another case,[26] it has been claimed that the decrease of $E_{\sigma=0}$ with Φ is not true as shown by correlating the metals within the same group, for instance Ga, In and Tl. In this case, in a different solvent (dimethylsulfoxide), it is even possible to show that $E_{\sigma=0}$ increases as Φ decreases. In water, as Figure 2 shows, $E_{\sigma=0}$ is almost constant within the above group of metals while Φ varies of up to 0.2 eV. However, the approach based on groups rather than on periods is unsatisfactory. It is of course possible to obtain any kind of correlation depending on the points correlated. But the choice must be based on sound arguments. In his theory on the variations of the bond strength and magnetic properties, Pauling correlated the properties of metals along a period and not down a group.[27] This is because a meaningful correlation involving electronic properties can be followed at best as a given electronic shell is progresively filled and not as filled shells of core electrons are added down a group. According to the significance of the
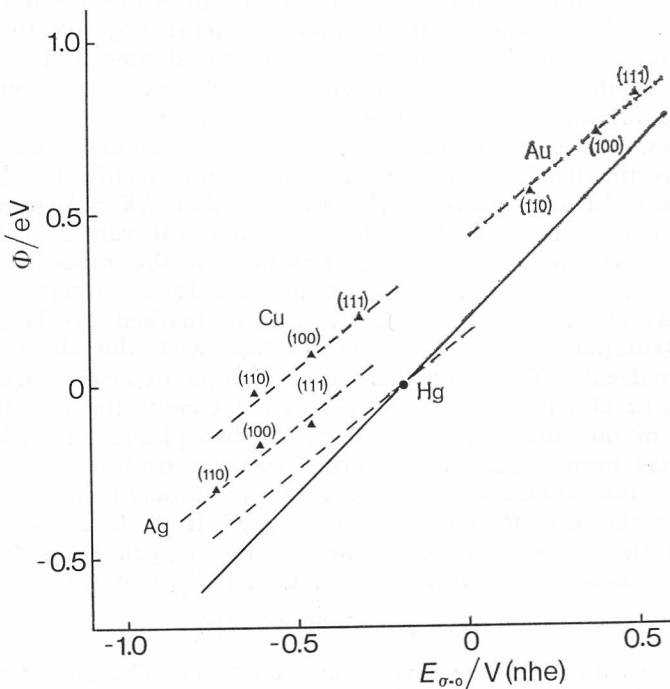

Figure 3. Plot of the electron work function vs the potential of zero charge (both relative to Hg) for the three main faces of Cu, Ag and Au.

Periodical Table, the metals in the same group possess similar chemical properties. Therefore, they should not be correlated with the aim to give evidence to a variation in the chemical properties.

The sd-metals, Cu, Ag and Au provide an illuminating example of the above situation. Since the surfaces of these metals are appreciably heterogeneous from a structural point of view,[10,26] polycrystalline samples do not provide results of quantitative significance.[28,29] Therefore, in Figure 2. the points for the (110) face (structurally homogeneous) have been reported. It can be seen that hese metals do not fall in any of the correlations found for the sp-metals. This is not surprising in view of the decisive difference in electronic structure. However, if the data for the main crystallographic faces of the three metals are correlated for each separate metal,[30] Figure 3. shows that they follow linear dependences which are probably parallel to those for the sp-metals. Therefore, eqn. (2) is still valid within each group of data, and its physical significance must be sought accordingly.

2.2. *The Term X*

The most direct information on the term X defined by eqn. (3) is obtained from Figure 2 with the aid of eqn. (2), which readily shows that for a given value of Φ, ΔX can be calculated from the distance of the point for the given metal from the straight line of unit slope passing through Hg. The early assumption[16] was that $\delta\chi_0$ was probably the same for all metals. Under similar circumstances, $\Delta X = g\,(\text{dip})_0^M - g\,(\text{dip})_0^{Hg}$, i. e. the deviation from the straight line measures the difference in water orientation at the two metals. If ΔX is negative, then $g\,(\text{dip})_0^M$ is more negative than $g\,(\text{dip})_0^{Hg}$ (that the latter is negative has been assessed several times[1]). The most ready consequence is that a stronger metal-water interaction is responsible for the enhanced orientation of the adsorbed molecule.

;   This view has been recently criticized on the ground that the role of $\delta\chi_0$ is underestimated.[31,32] However, this does not modify the phenomenological picture. In fact, instead of assuming that $\Delta X \simeq \Delta g\,(\text{dip})_0$, we can attach the same meaning to X itself. The numerical values of ΔX are not changed by modifying the meaning attached to the quantity. Therefore, a more negative value of X is taken to indicate a stronger metal-water interaction which is brought about by a more marked overlapping of the electron distribution tail at the metal surface with the electron cloud of the water molecule. The way this interaction is described, i. e. either in terms of $\delta\chi_0$ or of $g\,(\text{dip})_0$ or of both does not change the fact that a large modification of the surface parameters of the two phases unavoidably means that there has been a marked perturbation upon contact.

The way the significance of ΔX could be brought into evidence was suggested by the present authors years ago.[33] If X is a measure of the »affinity« of the surface for water through the oxygen atom, this quantity should bear a direct relationship to the heat (ΔX_{ox}°) of the reaction:

$$M\,(s) + 1/2\,O_2\,(g) \rightarrow MO\,(s) \tag{4}$$

which expresses the affinity of metal M for oxygen. The approach is in fact successful, as Figure 4 shows. ΔX increases as ΔH_{ox}° becomes more negative, i. e. as the affinity of M for oxygen increases.
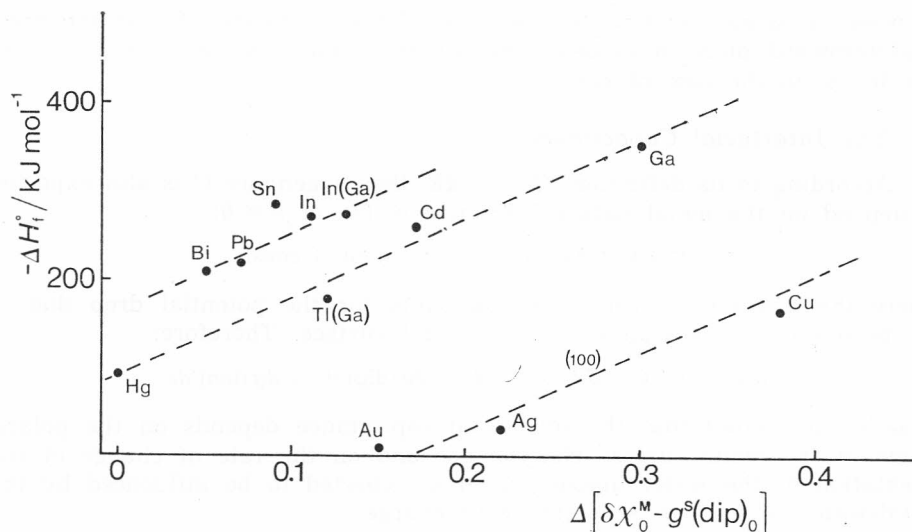
Figure 4. Plot of the term X — cf. eqn. (3) — vs the standard enthalpy of formation of the oxide MO — cf. eqn. (4). The data for Cu, Ag and Au refer to the (100) face.

Figure 4 is also illuminating from another point of view. It is clearly seen that Au, Ag and Cu fall in a separate group, which explains why the points for these metals cannot be grouped with the other sp-metals in Figure 2. Thus, the results for the sd-metals lead in fact to a revaluation of the term $\delta\chi_0$. Hydrophilicity in terms of ΔX can only be evaluated on a relative scale within a homogeneous series of metals. Since Au, Ag and Cu show fairly high values of ΔX but relatively low values of ΔX_{ox}°, which measures their affinity for oxygen (water), it ensues that most of ΔX is presumably due to $\delta\chi_0$ rather than to g (dip)$_0$. This necessarily implies that these metals possess very weak affinity for water molecules.[34] This conclusion is in fact corroborated by some pieces of independent experimental evidence. First of all, thermal desorption of water adsorbed on silver single crystal faces shows[35] that the metal-water interaction is not larger than the water-water bond strength in the liquid. This does not mean that the metal-water interaction is weak but that the orientation of water molecules at the metal surface is mainly governed by the interactions with the liquid phase.

Water molecules at the free surface of water are preferentially oriented so that a surface potential develops.[36] With reference to the situation at the free surface, a metal can be defined as hydrophilic if upon contact with the liquid phase it tends to increase the preferential orientation of water. If the latter does not change, the metal is hydrophobic, i. e. it may even enhance the local structure of the water surface. Thus, in respect to the intrinsic structure of the water surface, metals may be defined either as structure making or as structure breaking. In the case of silver, its surface behaves as a structure making surface. Therefore, Δg (dip)$_0$ should be small. Nevertheless, if water is adsorbed on silver from the gas phase, a large

decrease in work function is observed.[37] This is thought to be the most straightfoward piece of evidence in favour of the idea that ΔX is mostly due to $\delta\chi_0$ in the case of silver.

2.3. *The Interfacial Capacitance*

According to its definition, $C = d\sigma/dE$, the capacitance C is also expected to depend on the metal nature.[23] From eqn. (2), at $\sigma \neq 0$:

$$E = \Phi + \delta\chi_\sigma - g\,(\text{dip})_\sigma + g\,(\text{ion})_\sigma + const \tag{5}$$

where the additional term $g\,(\text{ion})_\sigma$ accounts for the potential drop due to the presence of free charges on the metal surface. Therefore:

$$dE/d\sigma = 1/C = d\,(\chi + \delta\chi)/d\sigma - dg\,(\text{dip})/d\sigma + dg\,(\text{ion})/d\sigma \tag{6}$$

Equation (6) shows that the interfacial capacitance depends on the polarization of the metal surface electron gas and on the rate of change of the orientation of the water dipole (which is expected to be influenced by the metal-water interaction strength) with charge.

Equation (6) describes the interfacial condenser in terms of three capacitors in series:

$$1/C = 1/C_M + 1/C_{or} + 1/C_{mol} \tag{7}$$

where C_M is the »metal« capacitance, C_{or} is determined by the orientational polarizability of water molecules and C_{mol} by their electronic and atomic polarizability. Although the idea of C_M was implicit already in the pioneering work of Rice[38], this term has been customarily neglected up to recent times. In such context, the interfacial capacitance has been assumed to be essentially determined by C_{or} and must therefore bear a definite relationship to the hydrophilicity.[1,23,39]

Figure 5 shows that C is in fact closely correlated to the »hydrophilicity« as expressed by ΔH_{ox}°. It is remarkable that all sp-metals are gathered in one group and that an almost exact inverse relationship exists[23] ($1/C$ is strictly linear vs ΔH_{ox}°). The results of Figure 5 thus suggest a new definition of »hydrophilicity«: hydrophilic metals are those with high C values.[40]

The above conclusion has been also questioned recently on different grounds. It may be not true that $1/C_M$ is negligible (infinite permittivity of the metal surface); therefore, C may be governed by the polarizability of the metal electrons rather than by that of water.[11-44] However, the interpretation of C does not modify the phenomenological situation which is represented by Figure 5. sp-metal with a high interfacial permitivity (polarizability) are hydrophilic irrespective of whether this is due to the metal or to water. Another criticism is that since thermal desorption show that the interaction of water with metal surfaces is generally weak,[35] the idea of »chemisorption«, which is sometimes put forward when referring to hydrophilicity,[39] is not supported by experiments. However, recent quantum chemical calculations[21,22] have substantially supported early suggestions about the orientation of water at metal surfaces. In particular, calculations show that the rotation of water molecules involves a very small work, so that thermal desorption might not be sensitive enough to discriminate between different metals.
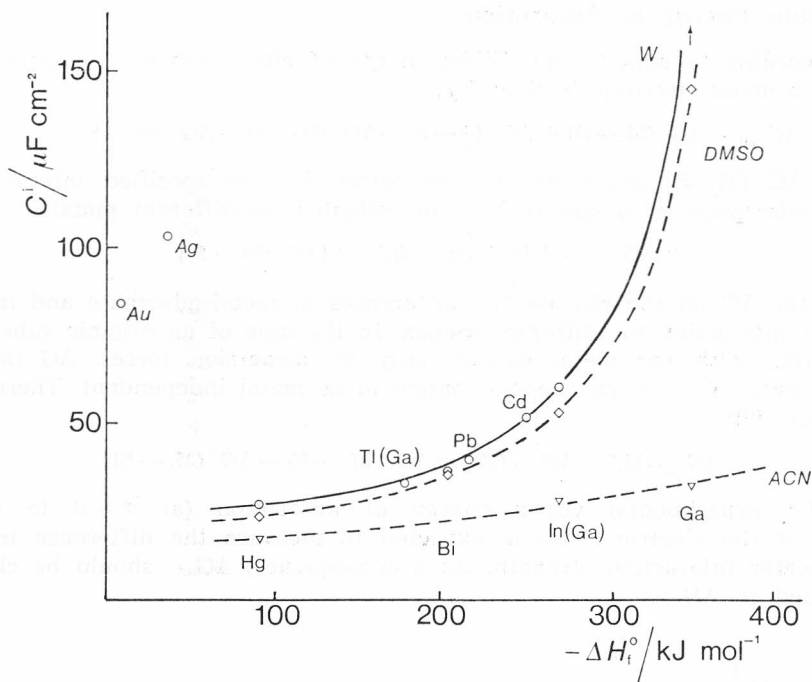
Figure 5. Plot of the inner layer capacitance in water (w), dimethylsulfoxide (DMSO) and acetonitrile (ACN) vs the standard enthalpy of formation of the oxide MO. The data for Au[58] and Ag[48] refer to the (210) and (110) face, respectively.

A more substantial criticism is based on the results for the sd-metals. Figure 5 shows that the points for Ag and Au fall dramatically far from the line gathering the sp-metals. The »hydrophilicity« scale based on the interfacial capacitance[23,40] is therefore not applicable to sd-metals. This simply means that these metals, as in Figure 4, cannot be grouped with the sp-metals, but it does not imply that the approach is generally invalid.

In the case of sp-metals, the bonding electrons are also those giving rise to the surface potential. Therefore, the polarizability of surface electrons and the metal-water interaction go parallel. In the case of sd-metals, the large $\delta\chi_0$ associated with a small ΔH_{ox}° may indicate that non-bonding (for the adsorbate) d-electrons take part in the surface potential. Therefore, a large $\delta\chi_0$ is not associated with an appreciable metal-water interaction. As a consequence a large value of C is not necessarily paralleled by a large »hydrophilicity«. These arguments imply that the electronic structure of the metals must enter as a primary factor in considering the interfacial interactions. As d-metals behave quite differently from sp-metals,[1,10] it is not surprising that the sd-metals should in turn behave somewhat intermediately. But this does not diminish the reasonableness of the approach with sp--metals.

2.4. *Gibbs Energy of Adsorption*

According to eqn. (1) the Gibbs energy of adsorption of a neutral species on a metal electrode is given by:

$$\Delta G^\circ_{ad} = \Delta G^\circ (M - B) + \Delta G^\circ (S - S) - \Delta G^\circ (B - S) - \Delta G^\circ (M - S) \qquad (8)$$

where $\Delta G (M - B)$ are Gibbs energy terms for the specified interactions. If the adsorption of a species B is investigated on different metals,

$$\Delta (\Delta G^\circ_{ad}) = \Delta [\Delta G^\circ (M - B)] - \Delta [\Delta G^\circ (M - S)] \qquad (9)$$

where the ΔG on the rhs are the differences in metal-adsorbate and metal-solvent interaction for different metals. In the case of an organic substance interacting with the metal surface only by dispersion forces, $\Delta G^\circ (M - B)$ can be assumed to a first approximation to be metal independent. Therefore, from eqn. (9):

$$\Delta G^\circ_{ad} (M_1) - \Delta G^\circ_{ad} (M_2) = \Delta G^\circ (M_2 - S) - \Delta G^\circ (M_1 - S) \qquad (10)$$

i. e., the experimental Gibbs energy of adsorption (at $\sigma = 0$ to avoid effects of the electric field) is expected to measure the difference in the metal-water interaction strength. As a consequence, ΔG_{ad}° should be closely correlated to ΔH_{ox}°.
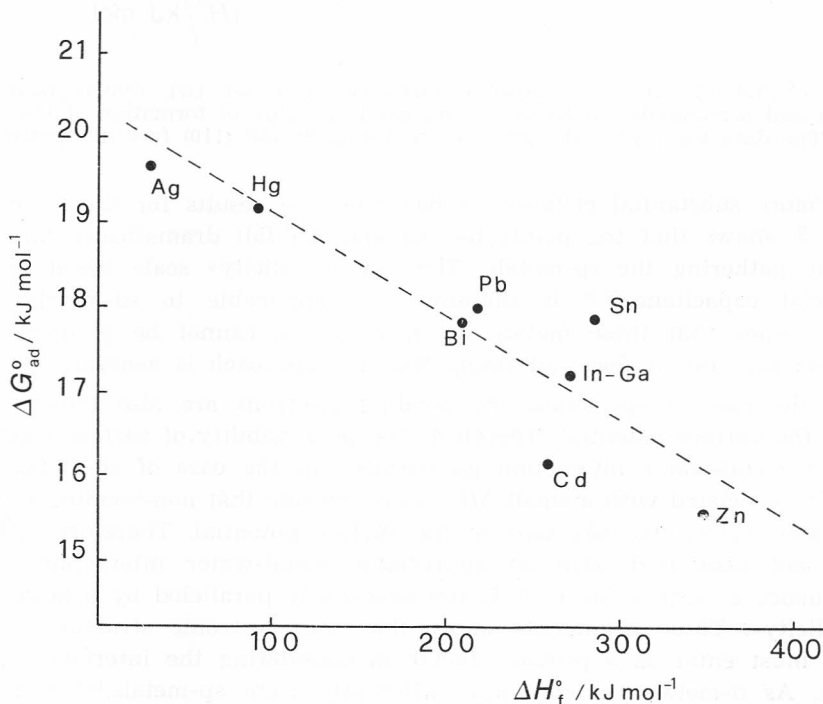

Figure 6. Standard Gibbs energy of adsorption of pentanol[1] as a function of the standard enthalpy of formation of the oxide MO. The value for Ag refers to the (100) face and has been extrapolated from that for hexanol.[59]

Figure 6 shows that this is in fact the case. ΔG_{ad}° for an organic adsorbate (linear aliphatic alcohol) which interacts with the solid surface through the hydrocarbon tail is seen to decrease linearly as the value of ΔH_{ox}° (viz. the »hydrophilicity« of the metal) increases. This indicates that adsorption progressively decreases as the removal of water molecules from metal surface becomes increasingly difficult. It is remarkable that the point for Ag now falls together with those for the other sp-metals. This is because ΔG_{ad}° and ΔH_{ox}° are both independent of the polarizability behaviour of non-bonding surface electrons. Thus ΔG_{ad}° and ΔH_{ox}° are more general parameters than X and C to define and evaluate the »hydrophilicity«.

3. ELECTRODE INTERFACE MODELING

Although modeling of the electrode interface to calculate capacitance curves can be traced back to 1961,[45] substantial progress has been made only since 1974,[39] as the idea of »hydrophilicity« was introduced into the models.

3.1. »Molecular« Models

So-called »molecular« models of water at metal electrodes[1] have been behaviour of sp-metals for which molecular models can give acceptable These models ignore the structure of the surface of the metal envisaged as a plane, perfectly conducting wall, and attribute any properties to the behaviour of a monolayer of water molecules. The details of the capacitance curves (C vs σ) could be reproduced by describing the monolayer as consisting of monomers and clusters. Only the former have been assumed to interact specifically with the metal surface (hydrophilicity). The various proposed models[1,46] differ mainly in the way the lateral interaction between water molecules is taken into account, which varies from neglect up to hydrogen bonding.[47]

Molecular models have been able to reproduce the main observable trends, i. e. an increase in C and g (dip)$_0$ with a strengthening of the metal--water interaction. Thus, a large value of g (dip)$_0$ (orientation) is brought about by a strong bond between the metal surface and the oxygen atom of the water molecule. Their major defect is that they include adjustable parameters. The agreement of their response increases with the number of these parameters, of course with a parallel decrease in the physical meaning.

The limitations of these models come out clearly as they are applied to sd-metals which have been observed (see above) not to conform to the behaviour of sp-metals for which molecular models can give acceptable results. In the case of silver, if the idea of hydrophilicity is accepted, then the models predict a »hump« in the capacity curve at positive charges[1] while the experimental one is observed[48] at $\sigma = 0$. While the latter observation means that no spontaneous preferential orientation in the molecular layer of water should be present, the models are unable to predict the observed high values of C if no specific chemical interaction is accounted for. Thus, in order to obtain the »hump« at $\sigma = 0$, hydrophobicity has been postulated[48] and the high value of C has been proposed to be due to a thinning of the interface because of the accomodation of water molecules in

hollow sites on the structured metal surface (in the case of liquid or homogeneous low-melting metals the surface can be envisaged as an ideal plane). However, the use of these models where the prevalence of the term $\delta\chi_0$ has been ascertained is physically inconsistent, and their apparent success is by no means a proof of their validity.

3.2. »Physical« Models

The revaluation of the role of $\delta\chi_0$ coincided with the birth[32] in 1981 of a new class of models[12] for the metal/solution interface where the electronic properties of the solid are appropriately taken into account through the »jellium« model,[43,50] i. e. on the basis of the electronic theory of metals. The introduction of these new ideas (which in fact were repeatedly touched upon in the past although on an empirical basis) has marked the transition of double layer modelling from a physico-chemical to a physical approach. Another group of models[51,52] have in fact been devoted to the description of the electrolyte solution close to a plane conducting wall by means of statistical mechanics. In these (»non-primitive«)[53] models, ions and solvent molecules are envisaged as hard spheres embedding point charges and point dipoles. The most advanced model for an interface is now considered to be that combining the »jellium« for the metal with the hard-sphere model for the solution.[43]

In the »physical« models the interaction between the metal and water molecules takes place through the electronic »tail« at the solid surface and the molecular dipole as they approach each other. According to these models the high interfacial capacitance of »hydrophilic« metals can be reproduced through the polarizability of the surface electron gas. However, they do not predict the high values of C for sd-metals, although the sequence for the main faces of single crystals is correctly obtained.[54] The metal-water interaction is not explicitly taken into account in chemical terms but it is implicitly included in the model, although its existence does not come out in the calculated parameters.

4. CONCLUSIONS

Analysis of a number of experimental parameters leads to a classification of the metals on the basis of their electronic structure. The modifications in the structure of the surface region brought about by the contact between the metal and the solvent are usually higher for sd-metals than for sp-metals. Results for single crystal faces of a given metal show that the interfacial structure is definitely face specific.

Comparison of electrochemical and gas phase data suggests that water molecules are associated like in the liquid also at the interface so that the intrinsic structure of the solvent still plays a major role in the surface region. Chemical interactions with the metal surface are as a rule relatively weak but small energetic changes can produce large variations in the electrical parameters. In a sense, it is possible to state that the electrode potential is a quantity whose components reflect and amplify chemical events occurring at the interface.

The theory of the electrode/solution interface, started with electrostatic models and developed through a chemical view of the complex interactions

in the boundary region, is now in the stage of »physical« models where the local properties of the metal surface are emphasized over the features of the layer of water molecules.* In particular, the role of the intrinsic structure of water in determining the interfacial behaviour is not adequately taken into account. Although the predictions of these models are encouraging, they do not give direct account of the chemical properties, so that any chemical viewpoint is lost. The best description of the interfacial region should however retain the concept of chemical bond, which means that a quantum chemical approach associated with the theory of metals may provide the best answer to the questions which still arise.

REFERENCES

1. S. Trasatti in B. E. Conway and J. O'M. Bockris, *Modern Aspects of Electrochemistry*, Vol. 13, Plenum, New York, 1979, p. 81.
2. R. Guidelli, *J. Electroanal. Chem.* **197** (1986) 77.
3. S. Trasatti, *J. Electroanal. Chem.* **65** (1975) 815.
4. M. D. Levi, A. V. Shlepakov, B. B. Damaskin, and I. A. Bagotskaya, *J. Electroanal. Chem.* **138** (1982) 1.
5. R. Amadelli, A. Daghetti, L. Vergano, A. De Battisti, and S. Trasatti, *J. Electroanal. Chem.* **100** (1979) 379.
6. R. Guidelli and M. L. Foresti, *J. Electroanal. Chem.* **197** (1986) 103.
7. P. Nikitas, *J. Electroanal. Chem.* **197** (1986) 29.
8. M. V. Sangaranarayanan and S. K. Rangarajan, *J. Electroanal. Chem.* **176** (1984) 119.
9. S. Trasatti, *J. Electroanal. Chem.* **123** (1981) 121.
10. S. Trasatti, *Electrochim. Acta* **28** (1983) 1083.
11. T. N. Andersen and J. O'M. Bockris, *Electrochim. Acta* **9** (1964) 347.
12. N. S. Razutikhina and A. N. Efremova, *Elektrokhimiya* **19** (1983) 1439.
13. A. Frumkin, B. Damaskin, N. Grigoryev, and I. Bagotskaya, *Electrochim. Acta* **19** 1974) 69.
14. S. Trasatti, *J. Chim. Phys.* **72** (1975) 561.
15. A. N. Frumkin and A. Gorodetzkaya, *Z. Phys. Chem.* **136** (1928) 451.
16. S. Trasatti, *J. Electroanal. Chem.* **33** (1971) 351.
17. N. D. Lang and W. Kohn, *Phys. Rev. B* **1** (1970) 4555.
18. S. Trasatti in J. O'M. Bockris, B. E. Conway, and E. Yeager (Eds.), *Comprehensive Treatise of Electrochemistry*, Vol. 1, Plenum, New York, 1980, p. 45.
19. J. M. Heras and L. Viscido, *Appl. Surf. Sci.* **4** (1980) 238.
20. D. E. Grider, K. Bange, and J. K. Sass, *J. Electrochem. Soc.* **130** (1983) 246.
21. A. Kuznetsov, J. Reihold, and W. Lorenz, *J. Electroanal. Chem.* **164** (1984) 167.
22. G. V. Kulkarni and S. K. Rangarajan, *J. Electroanal. Chem.* **196** (1985) 375.
23. S. Trasatti, *J. Electroanal. Chem.* **91** (1978) 293.
24. S. Trasatti, *Z. Phys. Chem.* **98** (1975) 75.
25. G. Valette, *J. Electroanal. Chem.* **139** (1982) 285.
26. I. A. Bagotskaya, Chan Ngok Hai, V. G. Boitsov, and V. E. Kazarinov, *Extended Abstracts. 37th ISE Meeting*, Vol. III, Vilnius, USSR, 1986, p. 224.

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* The latter prevail in fact in the temperature effects.[50] However, the models do not take properly account of the temperature behaviour of the electron gas at the metal surface.[55-57]

27. L. P a u l i n g, *Phys. Rev.* **54** (1938) 899; *J. Amer. Chem. Soc.* **69** (1947) 542; *Proc. Roy. Soc.* **A196** (1949) 343.
28. D. L a r k i n, *J. Electroanal. Chem.* **157** (1983) 123.
29. I. A. B o g o t s k a y a, B. B. D a m a s k i n, and M. D. L e v i, *J. Electroanal. Chem.* **115** (1980) 189.
30. S. T r a s a t t i, *Mater. Chem. Phys.* **12** (1985) 507.
31. W. S c h m i c k l e r, *Chem. Phys. Lett.* **99** (1983) 135.
32. J. P. B a d i a l i, M. L. R o s i m b e r g, and J. G o o d i s m a n, *J. Electroanal. Chem.* **130** (1981) 31.
33. S. T r a s a t t i, *J. Electroanal. Chem.* **54** (1974) 437.
34. G. V a l e t t e, *J. Electroanal. Chem.* **178** (1984) 179.
35. M. K l a u a and T. E. M a d e y, *Surf. Sci.* **136** (1974) 437.
36. J. E. B. R a n d l e s, *Phys. Chem. Lig.* **7** (1977) 107.
37. J. K. S a s s in *Trends in Interfacial Electrochemistry* (NATO Adv. Study Inst.), Riedel, Dordrecht (1986).
38. O. K. R i c e, *Phys. Rev.* **31** (1928) 1051.
39. B. B. D a m a s k i n and A. N. F r u m k i n, *Electrochim. Acta* **19** (1974) 173.
40. I. A. B a g o t s k a y a and A. V. S h l e p a k o v, *Elektrokhimiya* **16** (1980) 565.
41. J. P. B a d i a l i, M. L. R o s i m b e r g, and J. G o o d i s m a n, *J. Electroanal. Chem.* **143** (1983) 73.
42. M. A. V o r o t y n t s e v and A. A. K o r n y s h e v, *Elektrokhimiya* **20** (1984) 3.
43. W. S c h m i c k l e r, and D. H e n d e r s o n, *J. Chem. Phys.* **80** (1984) 3381.
44. G. A. M a r t y n o v and R. R. S a l e m, *Adv. Colloid Interface Sci.* **22** (1985) 229.
45. N. F. M o t t and R. J. W a t t s - T o b i n, *Electrochim. Acta* **4** (1961) 79.
46. W. R. F a w c e t t, *Isr. J. Chem.* **18** (1979) 3.
47. R. G u i d e l l i, *J. Electroanal. Chem.* **197** (1986) 77.
48. G. V a l e t t e, *J. Electroanal. Chem.* **122** (1981) 285.
49. S. T r a s a t t i, *J. Electroanal. Chem.* **150** (1983) 1.
50. W. S c h m i c k l e r, *J. Electroanal. Chem.* **150** (1983) 19.
51. S. L. C a r n i e and D. Y. C h a n, *Adv. Colloid Interface Sci.* **16** (1982) 81.
52. D. H e n d e r s o n, *Progr. Surf. Sci.* **13** (1983) 197.
53. D. H e n d e r s o n and L. B l u m, *J. Electroanal. Chem.* **132** (1982) 1.
54. D. H e n d e r s o n and W. S c h m i c k l e r, *J. Chem. Phys.* **82** (1985) 2825.
55. S. T r a s a t t i, *J. Electroanal. Chem.* **82** (1977) 391.
56. S. T r a s a t t i, *Appl. Surf. Sci.* **1** (1978) 341.
57. J. R. F a r r e l l and P. M c T i g u e, *J. Electroanal. Chem.* **163** (1984) 129.
58. A. H a m e l i n, Z. B o r k o w s k a, and J. S t a f i e j, *J. Electroanal. Chem.* **189** (1985) 85.
59. T. V i t a n o v and A. P o p o v, *Elektrokhimiya* **10** (1974) 1373.

SAŽETAK

Napredak u razumijevanju strukture granice faza metalna elektroda/otopina. Razvoj koncepta hidrofiliciteta

S. Trasatti

Jakost interakcije metal-voda (»hidrofilnost«) određuje kako strukturu međufaznog sloja, tako i energetiku adsorpcijskih procesa. Za seriju sp-metala može se primjenom fenomenološkog pristupa utvrditi skala »hidrofilnosti«. Na osnovi nedavnih rezultata za sd-metale (Cu, Ag, Au) pokazano je da oni ne odgovaraju tom modelu. To je uvjetovalo ponovno razmatranje faktora, koji određuju ponašanje elektrodnog međufaznog sloja. Posebno je potrebno uočiti, da je uloga površinskog elektronskog plina bila podcijenjena. »Fizikalni modeli« to naglašavaju, za razliku od »molekulskih modela« u kojima je odziv međufaze jednostavno ograničen na monosloj solvatiziranih molekula. U radu se naglašava da se takvim konceptima ne dolazi u sukob s fenomenološkim pristupom koji se zasniva na korelaciji nekoliko eksperimentalnih parametara s fizičko-kemijskim svojstvima metala.