CROATICA CHEMICA ACTA CCACAA 53 (2) 237—241 (1980)

CCA-1203

YU ISSN 0011-1643
UDC 546.212:541.61
Conference Abstract

Some Observations on the Structure of Water at an Ideal Metal-Solution Interface*

R. M. Reeves

Laboratoire d'Electrochimie Interfaciale, C.N.R.S., 1 place Aristide Briand, 92190 Meudon. France

Received December 26, 1979

The problem of describing the solvent structure at the solid-solution interface has been the subject of a large number of publications in recent years[1-3]. The majority of these models have been based on a simple dipole structure for the solvent and have used classical statistical techniques to calculate the pertinent parameters in the double layer, e. g. inner layer capacity and surface dipole potential. In effect, all are based on the original ideas of Watts-Tobin[4] and the differences in these various approaches are in the treatments of the solvent-solvent interaction terms. Some of the weaknesses in this work have been recently pointed out by Cooper and Harrison[5]. There are, however, a number of other fundamental weaknesses that should be noted;

a) It is not possible with these models to introduce, in anything but an arbitrary way, the specific interactions of the solvent molecules with the substrate although there is now a large body of evidence to show the importance and specificity of such interactions.[6]

b) The orientation of the solvent molecules in these models is chosen at the outset, that is to say the orientational distribution function is not a variable. The only attempt so far to avoid this restriction gave results which agreed poorly with experiment[7].

c) It has not yet been possible experimentally to show if the interactions of the primary solvent layer with the second solvent layer gives a significant contribution to the observed parameters although in colloid systems such interactions have often been suggested to explain phenomena. These interactions would be difficult to include in current models which already have to fit a large number of parameters to experimental data. These data, unlike spectroscopic data, do not have a high resolution response to the molecular parameters.

In this communication a tentative step in a new direction is proposed. One factor these models ignore is the rapidity of recent advances in the theory of the condensed state. If, for example, water is the typical solvent of interest, the recent publications of Stillinger and Rahman[8] and Frank[9]

---

[*] Based on a short contribution presented at the 5th »Ruđer Bošković« Institute's International Summer Conference *Chemistry of Solid/Liquid Interfaces*, Cavtat/Dubrovnik, Croatia, Yugoslavia, June 1979.

cannot be ignored. It is clear that the sophisticated models proposed for the solvent are still unrealistic in that many of the molecular contributions to the energy are lumped into constants, but they do present a basis for models significantly more realistic that the simple dipole. One example of these models is the so called ST2 structure[8]. This describes the spacial configuration of the water molecule, its charge distribution and its interaction energy using a tetrahedral structure. The charges on the corners of the tetrahedron are placed in such a way as to give the correct dipole moment. Coulomb's law can then be used to calculate the energy of interaction between these charges on different molecules. The problem of representing the central body forces between molecules canont be exactly solved in this model and these forces are approximated by a Lennard-Jones potential function. The physical model for the water molecule is shown in Figure 1, where $\Theta = 109° 28'$. The relationships describing the interactions between the molecules taken by pairs are;

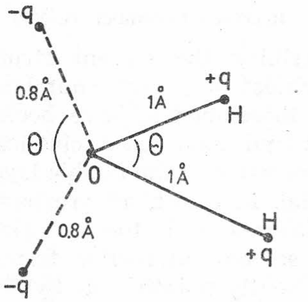

Figure 1. Structure of water molecule used for modelling.[8]

for the total energy,

$$V(1, 2) = V_{lj}(r_{12}) + S(r_{12})\, V_c(1, 2) \qquad (1)$$

for the Lennard-Jones energy V_{lj} where r_{12} is the oxygen-oxygen distance

$$V_{lj}(r) = 4\,\Theta\,[(\sigma/r)^{12} - (\sigma/r)^{6}] \qquad (2)$$

for the coulombic energy V_c (1, 2)

$$V_c(1, 2) = q^2 \sum_{\alpha\beta=1}^{4} (-1)^{\alpha+\beta}/d_{\alpha\beta}(1, 2) \qquad (3)$$

where d is the distance between charge α on molecule 1 and charge β on molecule 2, and α and β give the correct sign to the energy. There remains the so called modulation function $S(r_{12})$ which Stillinger and Rahman introduced to modify the contribution of V_c at short distances where V_{lj} must predominate. This takes the form,

$$S(r_{12}) = 0 \qquad (0 \leq r_{12} \leq R_L) \qquad (4a)$$

$$S(r_{12}) = \frac{(r_{12} - R_2)^2 (3R_U - R_L - 2r_{12})}{(R_U - R_L)^3} \qquad (R_L \leq r_{12} \leq R_U) \qquad (4b)$$

$$S(r_{12}) = 1 \qquad (R_U \leq r_{12}) \qquad (4c)$$

With Figure 1, these relationships are the basis for the ST2 water simulation. The problem of values for the constants in these relationships will be discussed later.

The overall aim of this model for the interface is to describe the properties of the interfacial solvent including the contribution from the metallic structure hence avoiding the arbitrary nature of earlier descriptions of these contributions. It is clear that a model for the solvent of this type, irrespective of its probable defects, would permit the incorporation of a specific surface structure in the model calculations. However, it is already clear that the inclusion of such a model in the earlier statistical approaches would not yield a tractable analytic solution. The model calculations have to be performed using modern numerical simulation techniques. With these, it is possible to envisage the correct coupling of the solvent molecule to the surface in the future. This requires the development of proper interaction functions for the metallic surface.

This study is more limited in scope and the interaction function with the surface was simplified for these preliminary calculations. The metallic surface was considered to be ideal and structureless. The interactions with this surface were split as they were split for the water-water molecule interaction into a central body (V_{lj}^{S}) and an image interaction (V_{c}^{S}). The V_{lj}^{S} was used to represent the interaction with an undeformable surface while the V_{c}^{s} was simply calculated on the basis of the classical image model with the inclusion of $S^{s}(r_{12})$ to stop unreasonable energies being calculated when the molecule is very close to the surface.

No attempt is made in this model to introduce the effect of electrode charge althoug this should be possible if the proper description of the metallic surface were available. The model chosen for the simulation comprises a monolayer of water molecules (8.10^{14} molecules cm^{-2}) arranged in a hexagonal lattice on the surface. As a Monte-Carlo technique was chosen, the movement of the molecules was restrained. Laterally this presents no problems if the constraint that moelcules cannot physically occupy the same space is applied but normal to the surface motion was restricted to a box of height 4.5 Å*. This effectively maintains the monolayer condition on the surface while allowing for interactions with molecules out of the monolayer plane. A microcanonical ensemble of 100 (10 × 10) molecules was used and the normal periodic boundary conditions were applied to this array. The array size was fixed at 35 Å × 35 Å.

The constants calculated by Rahman and Stillinger for the revised ST2 potential were used in the calculation of the energies of interaction of the water molecules, while with the surface, R_L was chosen to be 1 Å. The constant in V_{lj}^{s} is difficult to predict with certainty and a value 0.2 kJ mol^{-1} was chosen. The value of σ was also modified, a value of 1.75 Å being chosen.

The simulation was performed by setting the dipole orientation, the angle of rotation of the molecule around the dipole and the coordinates of the centre of the molecule using a random number generator. The array was subjected to a test of the constraints outlined above and corrected if necessary. The energy of the array was then calculated and its parameters stored. This was repeated for a large number of configurations to determine the range of energies produced by the model. Arrays whose energies lay outside the range 300 ± 5 °C were rejected. To determine the distribution function for the structure of the interfacial water molecules, a double correlation was performed first of all between the dipoles themselves using a ± 10° angle resolution and then between the dipole orientations and an energy map for the surface. Although this was not applied completely rigorously, it does enable, to a first approximation, the identification of structural features.

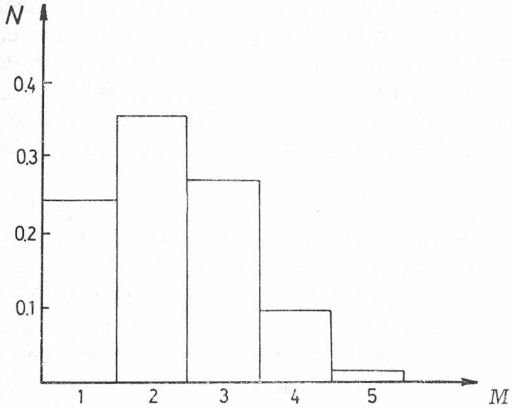

Figure 2. Distribution function for the orientation of water. N = normalised number of molecular 'groups' found in surface array. M = number of molecules in a molecular group on the surface.

The maximum in the distribution histogram occurs between associates of 2 and 3 molecules, a result which, probably fortuitously, agrees with that found using a model based on classical dipoles[10]. The statistics of this result are poor as only 26 arrays were available for analysis, the histogram being calculated from an average of the values obtained in all arrays for a particular configuration.

If this model has any validity it applies to an uncharged mercury surface.

The first and obvious comment to make on these results is that many more data are required and a proper statistical analysis has to be made of the results. The size of the surface array is too small. The influence of a specific configuration on the total configuration must be small otherwise periodic structuring in the ensemble occurs through the use of periodic boundary conditions. The definition of interactions with the surface needs improvement and the influence of the choice of $V_{1j}{}^{s}$ has to be studied. One factor missing in all but the rare gas simulations is the role of polarisability of the molecule in the formation of structures, a factor expected to be of greater importance in the anisotropic environment of the surface. This latter consideration also applies to the surface itself when approached by the solvent molecule.

The Monte Carlo approach adopted still imposes a degree of 2 dimensional structuring on the surface array and to overcome this we have attempted to use molecular dynamic methods to study the adsorption of the water and the subsequent formation of structures[11]. Stabilisation of the temperature (energy) in this case is the principal criterion but we have found that the surface has a destabilising effect on the molecular system so that as time progresses the energy performs large oscillations about a mean value. In addition the choice of interaction functions with the surface becomes critical as molecules can easily be 'lost' through the surface. Studies in this direction are continuing.

REFERENCES

1. R. M. Reeves, in: J. O'M. Bockris and B. E. Conway, (Eds.), *Modern Aspects of Electrochemistry*, Plenum, New York 1974, p. 239.
2. R. Parsons, *Trans, SAEST* **13** (1978) 239.
3. W. R. Fawcett, *J. Phys. Chem.* **82** (1978) 681.
4. R. J. Watts-Tobin, *Phil. Mag.* **6** (1961) 133.
5. I. L. Cooper and J. A. Harrison, *J. Electroanal. Chem.* **66** (1975) 85.
6. G. Valette and A. Hamelin, *J. Electroanal. Chem.* **45** (1973) 301.
7. K. B. Oldham and R. Parsons, *Elektrokhimiya* **13** (1977) 866.
8. F. H. Stillinger and A. Rahman, *J. Chem. Phys.* **60** (1974) 1545, J. S. Rowlinson, *Trans. Faraday Soc.* **47** (1951) 120.
9. F. Franks, *Water*, 4 volumes, Plenum, New York 1972.
10. W. R. Fawcett, private communication.
11. I. M. Williams and R. M. Reeves, unpublished data.

SAŽETAK

Neka opažanja o strukturi vode na idealiziranoj granici faza metal/otopina

R. M. Reeves

Postojeće teorije o strukturi vode na granici faza metal/otopina primjenjuju osnovne ideje o strukturi dvosloja, te o raspodjeli potencijala i o kapacitetu pojedinih slojeva. Međusobno se razlikuju uglavnom u članovima, koji se odnose na interakciju među molekulama otapala. Ipak, nijednoj od njih nije uspjelo razriješiti problem specifične interakcije otapala s površinom; nije razjašnjena raspodjela orijentacije tih molekula na površini, niti je eksperimentalno dokazan, teorijom zahtijevani, intenzitet interakcije primarnog sloja otapala sa sekundarnim.

LABORATOIRE D'ELECTROCHIMIE
INTERFACIALE
C.N.R.S.
MEUDON-BELLEVUE
FRANCE

Prispjelo 26. prosinca 1979.