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# The Structure of Water at Interfaces: A Brief and Selective Survey

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Present knowledge on the structure of water at air-water, metal-water and non-metal-water interfaces (the aqueous phase containing ions) is reviewed and discussed. The structural problem of interest is confined to the layers of water immediately at the interface, long range electrostatic forces being effectively screened by a diffuse layer of ions a few molecular diameters in half-thickness. A simple model of water in the monolayer next to a metal is outlined and shown to give a qualitative account of this region as far as electrical properties and their temperature coefficient are concerned. However, the latter is not a very sensitive test.

The subject of this lecture has been the source of almost as much controversy as the structure of liquid water and for similar reasons. The ability of water to form a great variety of intermolecular structures differing little in energy means that a high degree of sophistication is necessary in a theory that attempts to account for a wide variety of properties. This problem is exposed with great skill by H. S. Frank in volume 1 of the recently published treatise on water[1]. The general problem of water in interfaces was discussed from a range of points of view at a recent Solvay conference[2]. Here an attempt will be made to discuss the structure at interfaces between phases, the aqueous one containing ions. Under these circumstances the structural problem of interest is confined to the layers of water immediately at the interface, long range electrostatic forces being effectively screened by a diffuse layer of ions a few molecular diameters in half-thickness. The problem of the structure of water in the diffuse layer itself is more akin to the problem of water in a concentrated aqueous electrolyte, although, it must be admitted, a concentrated electrolyte of a type not met with in bulk phase since there is an excess of ions of one sign.

## THE AIR-WATER INTERFACE

The structure of this interface is of particular interest in marine science because a great deal of the interchange between the ocean and its environment occurs through this boundary[3]. The double layer at the surface plays an important role in the development of charges and the transfer of matter in splashing phenomena[4,5]. The orientation of water molecules probably plays no direct role in solutions as concentrated as sea water although it may influence the ionic distribution. Measurement of surface potentials indicates that the orientation of water is probably independent of ionic concentration up to values where there begins to be serious doubt about the individual activity coefficient[6], or at which specific adsorption effects become important. A variety of indirect methods led Frumkin, 20 years ago[7] to conclude that there was a small net orientation of water with oxygen towards the gas phase.

The most important of these indirect methods involve the measurement of the quantity known as the 'real free energy of solvation' of an individual ion. This is a directly measurable energy[8,9] analogous to the work function of an electron in a metal. The real free energy of solvation of an ion of species $i$ in a solvent of species $s$, $\alpha_i^s$ may be divided into

$$\alpha_i^s = \mu_i^s + z_i F \chi^s \tag{1}$$

where $\mu_i^s$ is the interaction energy between the ion and the bulk of the solvent, $z_i$ is the charge on the ion, $F$, Faraday's constant and $\chi^s$ the surface potential due to the double layer at the free surface of the solvent arising from the orientation of the solvent molecules. The first measurements of $\alpha_i^{H_2O}$ were made by Klein and Lange[10] in 1938 and these were used by Verwey[11] in 1942 to make the first quantitative estimate of $\chi^{H_2O}$ on the basis of values of $\mu_i^{H_2O}$ deduced from a model of the interaction of ions with bulk water. He obtained $\chi^{H_2O} = -0.5$ V which indicates a preferential orientation with the hydrogen atoms towards the gas phase. Similar results were obtained on the basis of a series of solvation models. However, it is clear from the fact that the values of $\alpha^{H_2O}$ are of the order of 400 kJ mol$^{-1}$ for simple monovalent ions, that extreme accuracy in the calculation of $\mu_i^{H_2O}$ from a model is required to obtain a reliable estimate of $\chi^{H_2O}$ since the surface term has a value of less than 50 kJ mol$^{-1}$ and probably much less than this. This point was clearly emphasised by Randles[12] who suggested that the best route to values of the two quantities on the right-hand side of (1) lay through the estimation of $\chi^s$. It must be noted that neither $\mu_i^s$ nor $\chi^s$ is directly accessible to measurement.

The most reliable route to $\chi^s$ appears to be through measurements of the temperature coefficient of $\alpha_i^s$:

$$\frac{d\alpha_i^s}{dT} = \frac{d\mu_i^s}{dT} + z_i F \frac{d\chi^s}{dT} \tag{2}$$

because the term $d\mu_i^s/dT$ which is the bulk contribution to the entropy of a single ion can be estimated with reasonable accuracy by methods suggested by Gurney[13]. This route was first used by Frumkin *et al.*[7] but more accurate results were obtained by Randles and Schiffrin[14] who obtained

$$d\chi^{H_2O}/dT = -0.43 \pm 0.02 \text{ mV K}^{-1} \tag{3}$$

Consideration of dipoles weakly oriented in the surface field leads to the suggestion that $\chi$ is inversely proportional to temperature. It is also probable that $\chi$ vanishes at the critical temperature of water. Recently on the basis of such arguments Randles[2] suggested that the most likely value was

$$\chi^{H_2O} = +0.08 \pm 0.06 \text{ V} \tag{4}$$

*i. e.* that water molecules are very slightly preferentially oriented with their oxygen atoms towards the gas phase. Some confirmation of this result is obtained from a comparison[15] of real free energies of solvation in $H_2O$ and in $D_2O$.

Up to the present time rather little work has been done on the structure of the surface of water, for comparison with the results obtained from the interpretation of experimental results described above. Fletcher followed an early crude estimate[16] of the $\chi$ potential with an improved version[17] in which the orienting force was due to the quadrupole moment of the water molecule[18]. At almost the same time Stillinger and Ben-Naim[19] described a more sophisticated model in which they assumed that, at temperatures just below the critical temperature water molecules would be oriented as a result of the quadrupole moment interacting with the shallow dielectric gradient. They showed that the sign of the $\chi$ potential was determined by the sign of the axial quadrupole moment and with values of the latter then available this sign agreed with that in equation (4). A somewhat unreliable extrapolation to room temperature led to a value within the range given in equation (4) but the authors claimed no strong validity for this. More recently experimental values for the quadrupole moments of water have been reliably determined[19,20] and calculated[21,22]. This should lead to a more reliable value of $\chi^{H_2O}$ but in fact it is difficult to reach a firm conclusion on the basis of this model because the quadrupole moment is a function of the coordinate system chosen. The appropriate centre of this system is presumably the centre of the assumed spherical envelope of the rotating water molecule. This does not seem to be known with enough certainty at present, if indeed the calculation can be done with any meaning at this level of approximation. It seems more likely at present that an approach from the point of view of molecular dynamics using computer simulation may be more profitable.

It may be noted that a similar difficulty arises in the calculation of the bulk solvation energy $\mu_i^s$ by the method proposed by Buckingham[23] which has been widely used in recent years. This may be one source of the disagreement between the estimates of $\chi^{H_2O}$ derived from $\mu_i^{H_2O}$ and $\alpha_i^{H_2O}$ and that of equation (4). A recent, very plausible, estimate[24] of $\mu^{H_2O}$ for the ferricinium ion on the other hand leads to a very satisfactory agreement with equation (4).

Optical methods show some promise for the investigation of the surface structure of water but so far have not been widely used. McBain *et al.*[25] concluded from the small ellipticity of reflected light at the Brewster angle that the transition layer between liquid water and its vapour was probably about one molecule thick. More recently Kinosita and Yokota[26] showed that this thickness was a function of temperature.

Randles[6] pointed out that the surface excess entropy of water at 25 °C

$$\begin{aligned} s = -(\mathrm{d}\gamma/\mathrm{d}T) &= 0.157 \text{ erg cm}^{-2}\text{ K}^{-1} \\ &= 0.157 \text{ mJ m}^{-2}\text{ K}^{-1} \end{aligned} \tag{5}$$

if ascribed to $1.7 \times 10^{-5}$ moles of water in a square metre of surface would be equivalent to a rise in entropy of 9.12 J K$^{-1}$ mol$^{-1}$. This is equal to the entropy increase in bulk water when its temperature is raised from 25 to 63 °C. Thus the decrease in structure seems to be relatively small and is probably confined to one or two molecular layers.

### THE METAL-WATER INTERFACE[27]

Serious speculation about the structure of water at mercury electrodes stems from Grahame's capacity measurements[28] which revealed clearly the 'hump' and particularly his study of its temperature dependence[29] although Frumkin[30] had discussed the orientation of water on different metals in connection with the concept of the point of zero charge. The 'dielectric' interpretation of the hump was proposed by Macdonald[31] and by Watts-Tobin[32]. The latter's model assumed that non-interacting water molecules could orient in two positions in a monolayer at the mercury-water interface. These two positions had equal and opposite dipole components perpendicular to the interface. One orientation was favoured as a result of the quadrupole moment, but the difficulties of such a calculation are similar to those discussed above. The potential drop across the monolayer of water was calculated as a function of the charge (regarded as uniformly distributed on either side of the monolayer) by adding the dipole potential to the potential across the molecular condenser in which the relative permeability was taken as equal to the square of the refractive index of water.

The dipole potential could then be expressed in reduced terms as

$$g = \tanh s \tag{6}$$

where

$$g = g_{\text{dipole}} \cdot (\varepsilon/\mu N_T) \tag{7}$$

and

$$s = (\mu/\varepsilon kT)\sigma \tag{8}$$

$\mu$ is the component of the dipole moment perpendicular to the interface, this was taken as $1/\sqrt{3}$ times the dipole moment of water. $\varepsilon$ is the permittivity of the water in the monalayer. $N_T$ is the number of water molecules per unit area of the monolayer, $k$ is Boltzmann's constant and $T$ the temperature. $\sigma$ is the charge on the metal, the charge on the solution being equal and opposite, and $g_{\text{dipole}}$ is the potential difference due to the oriented dipoles.

The total potential drop across the monolayer when the charge is $\sigma$ is the sum of $g_{\text{dipole}}$ and $g_{\text{ion}}$ where

$$g_{\text{ion}} = \sigma d/\varepsilon \tag{9}$$

if $d$ is the distance between the charged layers here taken as the thickness of the monolayer or the diameter of a water molecule.
If

$$\varepsilon/d = K_0 \tag{10}$$

the capacity of the inner layer with fixed orientation of water molecules, the reduced potential is

$$g_i = K s + \tanh s \tag{11}$$

with

$$K = \varepsilon^2 kT/\mu^2 K_0 N_T \tag{12}$$

If the reduced inner layer differential capacity $C$ is defined as

$$C = C^i/K_0 \tag{13}$$

where $C^i$ is the actual inner layer differential capacity, then this may be obtained from (11) as

$$C^{-1} = 1 - K^{-1} \operatorname{sech}^2 s \tag{14}$$

This gives a capacity curve with a hump superimposed on a constant capacity $K_0$. As the temperature is increased the hump is lowered and becomes broader. The introduction of a compressible inner layer in which $K_0$ is a function of charge as suggested by Macdonald[31] will give a closer fit to the experimental results[29]. Recently[33], Cooper and Harrison have pointed out that (14) can produce negative values of $C$ if $K < 1$ (see also ref. 46).

Bockris, Devanathan and Müller[34] modified this model in two principal respects. They allowed for dipole interaction between nearest neighbours in the layer and they assumed that the relative permeability of the water at fixed orientation was larger than the square of the refractive index for visible light. They chose a value of 6 which is approximately the value obtained from the extrapolation of the Cole-Cole plot for the permittivity of water in the microwave region[35]. Such a value gives a more reasonable result for $K_0$ with d equal to the diameter of a water molecule. However, there has been considerable discussion about the significance of this value. Recent results[36] seem to suggest that a process of very short relaxation time such as the rotation of molecules without hydrogen bond bending can account for the high frequency relaxation between 6 and the refractive index squared, but the controversy is not yet concluded[37].

Interaction was introduced by assuming that the energy of interaction between a pair of adjacent dipoles was $U_d$ if the dipoles are oppositely oriented and $-U_d$ if they are similarly oriented. The fraction of the $c$ nearest neighbours oriented in each way is put equal to the fraction of this orientation in the whole layer. Thus if the reduced energy of interaction with a set of nearest neighbours and oriented in the opposite way as the central dipole is defined as

$$U = U_d\, c/kT \tag{15}$$

the reduced energy of a given dipole is $UR$ with $R$ defined as

$$R = (N_+ - N_-)/N_T \tag{16}$$

where $N_+$ is the number of dipoles with their positive poles towards the solution and $N_-$ the number with the negative poles towards the solution. Application of Boltzmann statistics leads to the result that

$$R = \tanh\,(s - UR) \tag{17}$$

and that (6) is replaced by

$$g = \tanh\,(s - UR) \tag{18}$$

and (14) by

$$C^{-1} = 1 - K^{-1}\,\mathrm{sech}^2\,(s - UR) \tag{19}$$

$$= 1 - K^{-1}\left[\frac{1}{1-R^2} + U\right]^{-1} \tag{20}$$

Thus the presence of the term $U$ leads to a smaller contribution of the dipole orientation term to the inner layer capacity and Bockris *et al.*[34] claimed that this contribution was too small to account for the observed hump in the capacity whose origin must therefore be sought elsewhere as in the specific adsorption of ions. Later work suggests that the introduction of $U$ does not have such a marked effect. The model was extended in a later paper[38] to allow for solvent molecules oriented in two positions in which the dipoles were not equal and opposite.

The concept of unequal dipole orientations was taken up by Levine *et al.*[39] who also allowed for lateral interaction in a more generalized way by estimating the field due to the monolayer of dipoles at a particular dipole. At the same time they returned to a permittivity based on the optical refractive index which leads to poor agreement with the experimental results. Nevertheless, a main feature of their work is to show that the capacity hump need not occur at the point where $R = 0$ in contrast with the claim of Bockris *et al.*[34].

Damaskin and Frumkin[40] modified the Watts-Tobin model by applying it to small clusters of water molecules, for which some evidence exists from organic adsorption measurement[41,42]. In addition they assumed that individual water molecules may be chemisorbed on a positively charged metal surface. The extent to which the latter occurs depends on the hydrophilicity of the metal and the model gives a reasonable account of the shape of the capacity curve on various 'soft' metals. This model assumes a constant number of clusters with the chemisorbed water increasing the total density of water at the interface. High pressure measurements[43,44] have suggested such an increase in density but recent optical measurements[45] suggest that the increase is rather small though possibly sufficient for this model.

A more recent[46] model of this type suggests that the effect of the field at the interface is to break down the clusters into individual molecules as well as to re-orient them. This is expressed in terms of the difference in energy $U_{b,+}$ of a free molecule with its dipole oriented with the positive end towards the solution and a molecule in a cluster both at zero field due to charge. $U_{b,-}$ is a similar term for the free molecule oriented with the negative end of the dipole to the solution. Application of Boltzmann statistics to a monolayer containing a constant total number of molecules ($N_T$) leads to the result that (6) is replaced by

$$g = -D'/D \tag{21}$$

where

$$D = \exp \varrho s + \exp(-\varrho s) + A_+ \exp s + A_- \exp(-s) \tag{22}$$

$$D' = dD/ds \tag{23}$$

$$A_+ = \exp(-U_{b,+}/kT) \tag{24}$$

$$A_- = \exp(-U_{b,-}/kT) \tag{25}$$

and $\varrho$ is the ratio of the perpendicular component of the dipole moment per molecule in the cluster to the perpendicular component of the dipole moment of a free molecule. If $A_+ = A_- = 0$ and $\varrho = 1$ (21) reduces to (6). The reduced inner layer capacity as derived from (21) is

$$C^{\sim} = 1 - K^{-1}\{D''/D - (D'/D)^2\} \tag{26}$$

where

$$D'' = d^2 D/ds^2 \tag{27}$$

This model was shown[46] to reproduce with reasonable accuracy the experimental capacity curves for mercury in aqueous sodium fluoride as well as their temperature dependence, except at large negative charges where it may be necessary to invoke electrostriction[31]. The asymmetry of the curves produced is such that the maximum of the hump occurs at small positive charges whereas $g = 0$ at small negative charges, in agreement with the most probable interpretation of experimental results (see below). This asymmetry is due to the difference in values of $A_+$ and $A_-$ *i. e.* of $U_{b,+}$ and $U_{b,-}$.

The temperature dependence of the double layer capacity can be used to estimate the entropy of formation of the inner layer. This was calculated first by Hills and Payne[43] from Grahame's data[29]; the measurements and calculations have been repeated with essentially the same results[44,47,48]. Bockris and Habib[49] showed that the bell-shaped entropy-charge curves could be accounted for by the model of two position interacting water (equation 18). This is the two-dimensional analogue of a regular binary solution so that the entropy is the ideal energy of mixing of the two components (water in two positions).

$$\Delta S = -k\, N_T \{\frac{1}{2}(1+R) \ln \frac{1}{2}(1+R) + \frac{1}{2}(1-R) \ln \frac{1}{2}(1-R)\} \tag{28}$$

More recently Bockris and Habib[50] have carried out an elaborate absolute calculation of the entropy, using a model of dimers and single water molecules. The existence of dimers is based on the gas phase adsorption studies of Kemball[51] which in fact cannot be taken to exclude clusters with higher numbers of molecules. It is estimated that dimers form 68% of the layer and assumed that this fraction is independent of charge. The charge dependent part of the entropy arises from a term like (28) applied to the 32% of free molecules and from a variation of the librational entropy of the free molecules. Excellent agreement with experimental results is obtained.

It must be noted that the shape of the entropy-charge curve is not very sensitive to the model as the same shape is produced by any model in which a random mixture of a species oriented in two ways whether the species concerned is a cluster or a single molecule. The lack of sensitivity of the configurational entropy to the model is confirmed if the scale factors on this curve are calculated. The scale of the entropy change is determined by the total number of orienting species. This is $0.32\, N_T$ in the dimer model and $N_T/3$ in the cluster model if the clusters are taken to be trimers. The charge scale can be assessed by determining the width of the curve at half-height. Using the parameters quoted by Bockris and Habib with $U = 5$ as implied in their paper, this half width is found to be 14 $\mu$C cm$^{-2}$ whereas in the cluster model with the parameters previously chosen[46], it is 12 $\mu$C cm$^{-2}$.

It therefore appears to be necessary to apply the models to a wider range of phenomena. Capacity curves based on the dimer model of Bockris and Habib[49] do not appear to have been published, but the parameters used when substituted into (20) lead to a small hump only 15% above $K_o$ or 17.2 μF cm$^{-2}$ if $K_o$ is 15 μF cm$^{-2}$. This is consistent with their contention that water orientation is not the source of the hump. On the other hand the cluster model has been shown to account well for the capacity curves and their temperature coefficient in water[46,52] as well as for some types of non-aqueous capacity curves[52]. There is at present one qualitative discrepancy between the cluster model and experiment. This is the sign of the temperature coefficient of the dipole potential due to water. This quantity can be estimated from the temperature dependence of the potential of zero charge in much the same way as $d\chi^{H_2O}/dT$ is estimated. Randles and Whitely[53] estimated the temperature coefficient of the total dipole potential at mercury to be +0.56 mV K$^{-1}$ and it may be supposed that this is largely due to the orientation of water. The cluster model in its primitive form yields about —0.19 mV K$^{-1}$ for this quantity. It is possible to obtain a more reasonable value for this temperature coefficient by allowing for an asymmetric orientation of the clusters, but at the expense of agreement with other experimental features. There is clearly room for improvement although this model seems to explain the widest variety of phenomena at present.

The evidence for the existence of clusters is at present indirect and their use in a model of this type may be simply a more convenient way of representing the lateral interactions between molecules in the monolayer, analogous to the quasi-chemical method of treating interactions in solution. Nevertheless evidence from theoretical models of water is accumulating[54–56] that clusters are stable relative to individual water molecules, and various types of structures have been proposed. Most of these would have dipole moments and so a model involving dimers with no dipole moment[50] does not appear to be supported. Recent experimental[66] and theoretical[67] work on dimers indicates a large moment along the hydrogen bond with a small moment perpendicular to it. If this structure is assumed to be maintained at an interface and the hydrogen bond is parallel to the interface then the net moment of the dimer perpendicular to the interface may not be large. Nevertheless these results suggest that changes in configuration in the field are quite probable. Further work on the structures to be expected at an interface is desirable. An experiment approach which should throw some light on this problem is the study[57] of $D_2O$ solutions in comparison with $H_2O$.

## THE NON-METAL-WATER INTERFACE

Direct electrical measurements of double layer capacity are not possible for the interface between an aqueous electrolyte and a nonconducting solid. Even with semiconductors, unless the carrier density is so high that the surface becomes degenerate, the effect of the inner part of the double layer is swamped by the contribution of the space charge layer to the total capacity. However the capacity has been deduced for colloid systems like AgI especially by Lyklema[58] and the water structure discussed in terms of the same model by Levine *et al*[59]. The evidence for water structure is more by analogy with that at mercury electrodes rather than on direct evidence.

An interesting system of this type where more direct evidence is available is that of water layers intercalated in clay structures. Here it is possible to examine the structure more directly by X-ray, ir and NMR as well as by dielectric constant measurements. The regular structure of water is hexagonal[60] and the dielectric constant is similar to that of ice[61]. However ir[62] and NMR[63] measurements lead to the suggestion that the degree of dissocation of water is enhanced considerably in this situation which is therefore somewhat different from that in bulk ice. It is suggested that this is due to the high electric field. The implications of this for other interfaces have not yet been explored.

The interface between aqueous electrolytes and non-polar-liquids is perhaps closest to the air-water interface in character. Little clear evidence is available on the structure of water at this interface although a great number of experiments have been done[64]. A careful study of the interfacial tension of the hexane-water interface by Franks and Ives[65] indicated the presence of a markedly non-linear dependence with an inflection at about 33 °C which they relate to the bulk structure of water.

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## SAŽETAK

### Struktura vode na granicama faza: sažeti i odabrani pregled

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Predmet ovog predavanja predstavlja isto toliko kontroverzija kao i struktura vode u homogenoj fazi, i iz istih razloga. Svojstvo vode da tvori mnoštvo različitih intermolekularnih struktura, vrlo blizih energija, zahtijeva ujedno vrlo visok stupanj razrađenosti i složenosti teorije, koja bi pokušala objasniti svu raznolikost njenih svojstava. Ovdje je dat pregled i diskusija sadašnjeg znanja o strukturi vode u međufazi na granicama faza zrak—voda, metal—voda i nemetal—voda, pri čemu vodena faza sadržava ione. U tim uvjetima najinteresantniji strukturni problem posvećen je slojevima vode u samoj međufazi, gdje su elektrostatske sile većeg dometa zaklonjene difuzijskim slojem iona poludebljine nekoliko molekularnih diametara. Problem strukture vode u difuzijskom sloju sličan je problemu strukture vode u koncentriranim vodenim otopinama elektrolita, s tom razlikom da je ovdje prisutan suvišak iona istog naboja.

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