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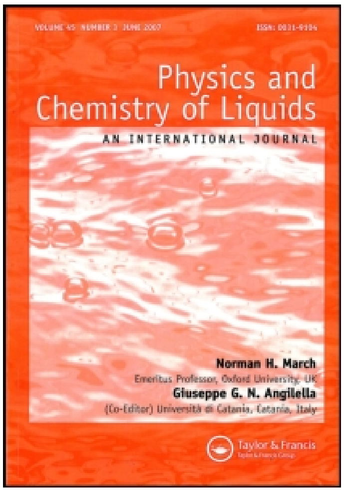

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Structure at the Free Surface of Water and Aqueous Electrolyte Solutions

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Structure at the Free Surface of Water and Aqueous Electrolyte Solutions†

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INTRODUCTION

During the past 20 years or so one of the regions of conspicuous growth in the field of physical chemistry has been the study of the structure and behaviour of water and aqueous solutions. There are practical reasons, for example technical and biological, for this interest, but it is also true that the complexity of water as a liquid provides its own motive to the research worker. It is unlikely that we would spend so much time in the study of water if it were as simple a liquid as Argon. However, strange though the behaviour of liquid water is, it is probably not as strange as it has sometimes been thought to be. The thermal "anomalies" of water[1] and the abnormal "Poly-water"[2] seem rather likely to fade out of the scientific scene, as have other stimulating but nonviable scientific myths.

In the proliferating literature on the structure and behaviour of water and aqueous solutions, studies of the gas-liquid interface have not been conspicuous. In the preface to a recent monograph on water[3] the authors remark that "... thermal conductivity and surface tension of the liquid are not discussed because they have not yet contributed to our understanding of the liquid structure." This is fair comment but it is nevertheless a fact that surface properties are of importance in the assessment of some aspects of ion-solvent interaction in electrolyte solutions. The energy (and entropy) of hydration of ions is only known thermodynamically for pairs or groups of ions of zero net charge. The division of the combined energy into single-ion

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† Presented at XV Solvay Conference on "Electrostatic Interactions and the Structure of Water," Brussels, 1972.

hydration energies depends on rather uncertain non-thermodynamic arguments. Almost certainly a more reliable route to these quantities is to use the "real" single-ion hydration energies which are measurable, and to subtract from these the contribution due to the surface potential of water. This is discussed in the final section of this Report. Surface studies of electrolyte solutions also yield information on the relative ease of approach of different kinds of ion to the surface. This depends very much on the character of the hydration shell of the ion and if more precise data on surface properties were available it would probably contribute to a better understanding of the structure of ionic hydration shells. In this Report, therefore, I have concentrated on two main fields: (1) studies of the gas–liquid interface of water and of aqueous solutions of simple inorganic electrolytes, aimed at an understanding of the structure of the interface itself; (2) the application of such studies, and in particular of surface potentials, to the estimation of single ion hydration energies and to related problems.

1 THE GAS–LIQUID INTERFACE

1.1 General consideration

At a gas–liquid interface there is a transition from the density, composition and structure of one stable bulk phase to that of the other. For a pure substance the transition can be defined in terms of only one variable, the density. Molecular and kinetic considerations require that the transition cannot occur abruptly at a geometric surface but through a transition zone of finite thickness. The intermediate densities existing in this zone would not be stable as a bulk phase. The point is illustrated in Figure 1. It is a familiar fact that on a P–v diagram for a pure substance the liquid and vapour isotherms for any sub-critical temperature can be linked by a continuous isotherm, e.g. by using the van der Waals equation. The region ABCD in Figure 1 represents the behaviour of a hypothetical single phase of density (or molar volume) intermediate between those of the co-existent stable phases, A and D. The molar Helmholtz free energy f of such a hypothetical phase is indicated in Figure 1 by region XYZ of the f curve. The straight line XZ represents the value of f for one mol of substance present as two phases. A single phase of density anywhere in the range A to D is thermodynamically unstable relative to two phases, but whereas ranges A–B and C–D are to some degree experimentally accessible as metastable states of the liquid or vapour, the range B–C represents a density range of absolute or mechanical instability since here $\mathrm{d}P/\mathrm{d}v$ is positive. In the corresponding region of the f curve, $(\partial^2 f/\partial v^2)_T$ is negative. The lower the temperature the more positive becomes $\mathrm{d}P/\mathrm{d}v$, and

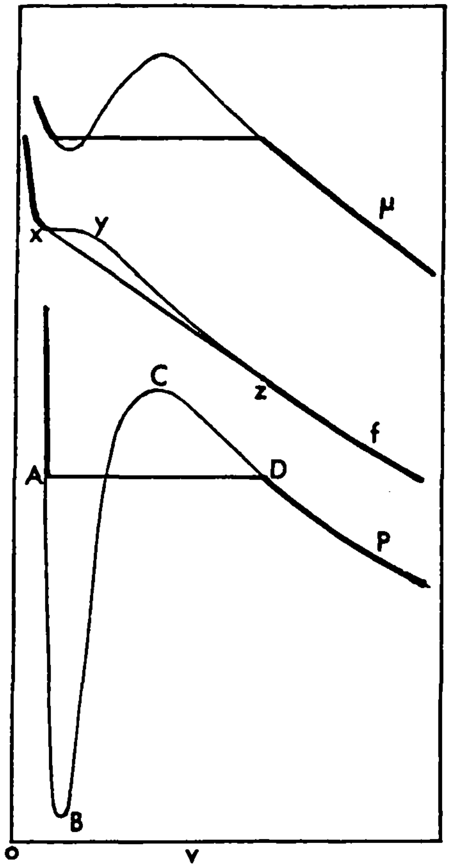

FIGURE 1 P–v diagram for a pure fluid below its critical temperature, together with the interpolated continuous isotherm for a hypothetical single phase.
Upper curves: *f*-Helmholtz free energy, μ-chemical potential, also with interpolated continuous curves for a hypothetical single phase.

the more the free energy of the single phase (in the XYZ range) exceeds that of the two phase system. Thus, as the temperature is lowered the more constricted we should expect the transition zone to become.

Theories of the structure and thickness of the transition zone are primarily based on statistical-molecular calculations, but as yet these can only be made quantitative for simple systems such as the interface between an inert gas and its liquid. In early calculations of surface tension[4–7] it was assumed that the change of density from that of the liquid to that of the vapour occurred abruptly, or at the most through a single molecular layer. Later calculations[8–10] permitted a transition zone more than a monolayer thick to be

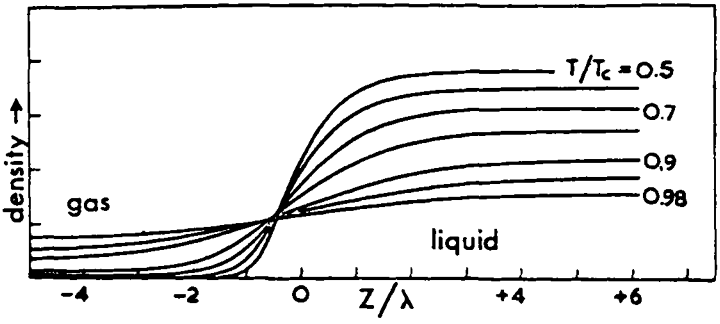

FIGURE 2 Curves of density in the liquid–vapour transition zone of a simple fluid at several reduced temperatures; λ = distance between nearest neighbour molecules in the bulk liquid After T. L. Hill.[9]

considered, and the number of layers involved and the approximate density gradient emerged as part of the results of the theory. The form of the density profile for a simple (monatomic) fluid for several reduced temperatures (i.e. T/T_c where T_c = critical temperature) according to Hill's[9] calculations is shown in Figure 2. Hill's method of calculation may slightly exaggerate the diffuseness of the zone and other methods[8,10] make it rather more compact. But it is fairly safe to assume that at the interface between a monatomic liquid and its vapour at $T \sim T_2/2$ the transition zone is between two and three molecular diameters thick, increasing with increasing temperature.

An interesting quasi-thermodynamic treatment of the transition zone has been attempted by Cahn and Hilliard.[11] They assumed the time-average density, ρ, in this zone to vary continuously along the normal (z) to the interface and they took the local molecular free energy f to be a function not only of ρ (as indicated by the f curve in Figure 1) but also of $(\mathrm{d}\rho/\mathrm{d}z)^2$ and of $\mathrm{d}^2\rho/\mathrm{d}z^2$. The free energy of the whole zone was calculated, the condition for a minimum found and from this the surface tension was deduced. An absolute value of surface tension (γ) could not be found but the calculated temperature dependence of γ was in good agreement with experiment. The method is admittedly crude but brings out the point that if concepts such as molecular free energy or chemical potential are meaningful in the liquid–vapour transition zone then they must depend not only on the value of ρ at a point but also on its derivatives with respect to z. An expression for the thickness, d, of the transition zone for a simple fluid was also obtained:

$$\frac{d}{\lambda} \simeq 2\left(\frac{T_c}{T_c - T}\right)^{1/2} \tag{1}$$

where λ is the average intermolecular distance between nearest neighbours in the bulk liquid. This leads to $d \sim 3\lambda$ at $T = T_c/2$, a similar value to that obtained by Hill (Figure 2) and with a similar temperature dependence.

We have been considering the transition zone as though it were uniformly planar though it has been emphasised by Drost-Hansen[1a] that the surface of a liquid is not quiescent but is subject to thermal motion and frequent exchange of molecules with the vapour phase. The "roughness" of a liquid surface can be regarded as the combined effect of a whole spectrum of waves (capillary, rather than gravitational) of wavelength varying from the size of the whole surface down to molecular dimensions. The existence of such waves can be confirmed by their effect in causing the scattering (as well as specular reflection) of light by a liquid surface.[12] Surface irregularities of molecular dimensions can be regarded as due to the superimposing of short-wavelength waves, but it is not easy to deduce the magnitude of the displacements. An approximate estimate can be obtained from a very simple calculation. Suppose that a local elevation (or depression) has the shape of a segment of a sphere (Figure 3). It is easily shown that the excess area of this "hump"

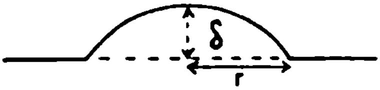

FIGURE 3 Model for a "hump" of molecular dimensions in a liquid surface.

(or hollow) compared with the plane surface is $\pi\delta^2$, independent of r (δ and r as in Figure 3). Hence the local excess energy is $\pi\delta^2\gamma$. This must come from a random local energy surplus and the problem is simply to find what magnitude of hump such local energy deviations can produce. Assuming a simple lattice model for the liquid with λ as average intermolecular distance between nearest neighbours, we can take λ^2 as the surface area per molecule. Then the number of surface molecules in the area, πr^2, of the hump is

$$N = \frac{\pi r^2}{\lambda^2} \tag{2}$$

The average total energy of vibration along the normal to the interface of these N molecules is NkT and the standard deviation from the mean is roughly $N^{1/2}kT$. A deviation greater than $2N^{1/2}kT$ has a probability of less than 0.05, so we will calculate the size of hump that could be formed by this amount of energy. Using Eq. (2) for N, this is given by

$$\gamma\pi\delta^2 = 2\pi^{1/2}\left(\frac{r}{\lambda}\right)kT \tag{3}$$

For the purpose of this estimation we will use the "Eötvos Law" for γ

$$\gamma v_m{}^{2/3} = K_\epsilon(T_c - T) \tag{4}$$

where v_m is the molar volume of the liquid and K_e is the Eötvos constant, averaging, for most liquids, 2.1 ergs deg^{-1} $\text{mol}^{-2/3}$. For our model of the liquid

$$v_m = N_A \lambda^3 \tag{5}$$

where N_A is Avogadro's number. Using Eqs. (3), (4) and (5) and inserting numerical values,

$$\frac{\delta}{\lambda} = 0.73\left(\frac{T}{T_c - T}\right)^{1/2} \frac{r}{\lambda}^{1/2} \tag{6}$$

For a liquid-vapour interface at $T = T_c/2$ Eq. (6) shows that if

$$r = 2\lambda (N \sim 12 \text{ molecules}),\ \delta \simeq 1.03\lambda$$
$$r = 3\lambda (N \sim 28 \text{ molecules}),\ \delta \simeq 1.26\lambda$$
$$r = 6\lambda (N \sim 80 \text{ molecules}),\ \delta \simeq 1.63\lambda$$

and so on. The result implies that surface irregularities in regions of molecular dimensions rarely reach more than $\frac{3}{2}$ molecular diameters in height or depth. In fact, since the liquid–vapour transition zone at $T = T_c/2$ is 2 or 3 molecules thick, such irregularities merely form part of the diffuseness of the zone. Comparison of Eqs. (6) and (1) shows that the calculated temperature dependence of the zone thickness, and the size of the irregularities, are rather similar.

We need next to extend our picture of the gas–liquid interface from simple monatomic fluids to more complex fluids, and in particular to water. Realistic molecular-statistical calculations are not yet practicable for such complex fluids and the best way to proceed is to compare the thermodynamic properties of the gas–liquid interface for complex fluids with the corresponding properties for simple fluids. This we do in the next section.

1.2 Thermodynamics of the Gas-Liquid Interface

The thermodynamic properties of the gas–liquid interface of a pure (i.e. single component) fluid which are most easily related to molecular structure are the surface excess energy $u^{\sigma e}$, and the surface excess entropy, $s^{\sigma e}$. Both of these should be defined as surface excesses relative to the *liquid phase*, a point which is not always made clear. I shall give here only a brief and simplified derivation of the equations defining these quantities. There are several detailed and authoritative expositions[13–16] of the thermodynamics of interfaces which can be consulted for details.

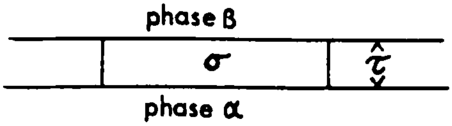

FIGURE 4 Model for phase σ.

The conceptually simplest model on which the thermodynamics of an interface may be based is the "surface phase" model proposed by Verschaffelt and developed by Guggenheim†.[13] The surface phase is a layer of finite thickness, τ, bounded by surfaces parallel to, and one on each side of, the physical transition zone (see Figure 4). We consider a portion of this phase containing an area A of interface and refer to it as phase σ. The fundamental differential equation for the energy U^σ of phase σ in a multi-component system, is[13]

$$\mathrm{d}U^\sigma = T\mathrm{d}S^\sigma - P\,\mathrm{d}V^\sigma + \gamma\,\mathrm{d}A + \Sigma\,\mu_i\,\mathrm{d}N_i^\sigma \tag{7}$$

where S^σ and V^σ are the entropy and volume of phase σ, N_i^σ is the number of molecules of component i present in σ, and μ_i is the molecular chemical potential of i. At equilibrium μ_i is the same in phase σ as it is in the two bulk phases. Integration of Eq. (7) (at constant thickness, τ, of σ) leads to

$$U^\sigma = TS^\sigma - PV^\sigma + \gamma A + \sum_i N_i^\sigma \mu_i \tag{8}$$

and we can define two free energies

$$\mathcal{G}^\sigma = U^\sigma - TS^\sigma + PV^\sigma \tag{9}$$

and

$$G^\sigma = \mathcal{G}^\sigma - \gamma A = \sum_i N_i^\sigma \mu_i \tag{10}$$

Differentiating (9) and (10) and using (7) we have

$$\mathrm{d}\mathcal{G}^\sigma = -S^\sigma\,\mathrm{d}T + V^\sigma\,\mathrm{d}P + \gamma\,\mathrm{d}A + \Sigma\mu_i\,\mathrm{d}N_i^\sigma \tag{11}$$

and

$$\mathrm{d}G^\sigma = -S^\sigma\,\mathrm{d}T + V^\sigma\,\mathrm{d}P - A\,\mathrm{d}\gamma + \Sigma\mu_i\,\mathrm{d}N_i^\sigma \tag{12}$$

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† Ono and Kondo[14] and Defay, Prigogine and Bellemans[16] prefer to use the classical Gibbs treatment but Eriksson[15] uses the surface phase model. All the thermodynamically rigorous results obtained by the two methods are identical.

From Eq. (12) a chemical potential† in phase σ is formally the partial molal G^σ (not $\mathscr{G}^\sigma$):

$$\mu_i^\sigma = \left(\frac{\delta G}{\delta N_i^\sigma}\right)_{T,P,\gamma,N_j^\sigma} \tag{13}$$

From Eq. (10)

$$\lambda A = (\mathscr{G}^\sigma - \Sigma N_i^\sigma \mu_i) \tag{14}$$

and for a single component system

$$\gamma A = \mathscr{G}^\sigma - N^\sigma \mu \tag{15}$$

Since $N^\sigma\mu$ is the Gibbs free energy of N^σ molecules in *either* bulk phase, γ is the surface excess free energy per unit area with respect to either bulk phase.

Referring now to a single component system we differentiate Eq. (15) with respect to T keeping the area A constant. The system (one component, two phases) is univariant, so change of T implies change of P and, because of thermal expansion, if A and τ are constant N^σ must also change. Hence, when differentiated, Eq. (15) becomes

$$A\,\mathrm{d}\gamma = \mathrm{d}\mathscr{G}^\sigma - N^\sigma\,\mathrm{d}\mu - \mu\,\mathrm{d}N^\sigma$$

which together with Eq. (11) gives

$$A\,\mathrm{d}\gamma = -S^\sigma\,\mathrm{d}T + V^\sigma\,\mathrm{d}P - N^\sigma\,\mathrm{d}\mu \tag{16}$$

The change in μ must be defined with reference to one or other of the bulk phases, say phase α,

$$\mathrm{d}\mu = -s^\alpha \mathrm{d}T + v^\alpha \mathrm{d}P$$

where s^α and v^α are the molecular entropy and volume in this phase. Using this, Eq. (16) becomes

$$A\,\mathrm{d}\gamma = -(S^\sigma - N^\sigma s^\alpha)\mathrm{d}T + (V^\sigma - N^\sigma v^\alpha)\mathrm{d}P \tag{17}$$

If we limit the thickness of phase σ to the density transition zone (which is reasonable since this is the site of the surface tension) the average density

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† In contrast, Eriksson[15] uses $(\delta\mathscr{G}^\sigma/\delta N_i^\sigma)_{T,P,n_j^\sigma} = \mu_i + \gamma a_i$ as his definition of chemical potential in σ. The definition we have used implies that μ_i is the same in σ as in the bulk phases, and moreover should be constant through the transition zone in σ. The curve for μ in Figure 1 shows the variation of μ with density for the hypothetical single component single phase to which the continuous P–v isotherm applies. To resolve this apparent contradiction, we recall Cahn and Hilliard's assumption (p. 00) that the local Helmholtz free energy f is a function of the derivatives of ρ with respect to z, as well as of ρ itself. The same must apply to the local value of μ, hence despite the variation of μ with ρ depicted in Figure 1, μ can nevertheless be constant through the transition zone because of its dependence on $\mathrm{d}\rho/\mathrm{d}z$ and $\mathrm{d}^2\rho/\mathrm{d}z^2$ also.

in it is near the arithmetic mean of the densities of the liquid and vapour phases. Then if we choose α to be the liquid phase, V^σ is about double $N^\sigma v^\alpha$ and the pressure dependent term on the right hand side of Eq. (17) can be neglected in comparison with the other term. This would not be so if we chose α to be the vapour phase.

We shall therefore simplify Eq. (17) by using the liquid as the reference phase, α. Also we shall standardise the area by using the molecular area as defined empirically (see Eq. 5) by

$$a = \lambda^2 = \left(\frac{v_m}{N_A}\right)^{2/3} \tag{18}$$

Thus

$$a.\frac{\mathrm{d}\gamma}{\mathrm{d}T} = -\frac{a}{A}(S^\sigma - N^\sigma s^\alpha) = -s^{\sigma e} \tag{19}$$

where $s^{\sigma e}$ is the molecular surface excess energy relative to the liquid phase. Corresponding to Eq. (19) we have also

$$a\gamma = g^{\sigma e} \tag{20}$$

and

$$a\left[\gamma - T\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right] = u^{\sigma e} \tag{21}$$

Both $u^{\sigma e}$ and $s^{\sigma e}$ may be related to the molecular structure of the gas–liquid interface. We start with the simplest model of the interface between a monatomic liquid and vapour, which uses a lattice model for the liquid and assumes an abrupt change of density from the uppermost liquid layer to the vapour. If the liquid lattice is face-centred cubic and the surface is a 1,1,1 face, each surface molecule has only 9 nearest neighbours compared with 12 for a molecule in the bulk-liquid.[5,7,16] It follows that to bring a molecule to the surface should require $\frac{3}{12}$ of the energy required to vaporise it. Even though co-ordination numbers in monatomic liquids at $T \sim 0.6T_c$ are 8 or 9 rather than 12,[17] the fraction of nearest neighbour bonds broken on bringing a molecule to the surface is probably similar. Thus $u^{\sigma e}/\Delta u$ev. should be ~ 0.25 where Δuev. is the energy of evaporation per molecule. In fact this ratio for simple fluids (the inert gases) is 0.48 at $T = 0.6T_c$ and increases with increasing temperature. The discrepancy is easily explained. In the simple model described no allowance is made for the lower density in the transition zone than in the bulk liquid. Although such an expansion of the liquid implies an increase of potential energy because of the work done against intermolecular forces, there can be a decrease of free energy because of the increased entropy of the expanded liquid. At equilibrium the free energy is minimised. Thus while $a\gamma(=g^{\sigma\sigma})$ must be less than $u^{\sigma\sigma}$ calculated with neglect of surface zone expansion (i.e. Δuev./4), the experimental $u^{\sigma\sigma}$ should be greater. The first part of this statement appears to be true of all liquids; the second part is true only of liquids classified as "normal."

The classification of fluids as "normal" or otherwise was elaborated by Riedel[18] and by Pitzer and co-workers.[19] It is based on the degree to which a substance in its liquid and vapour states conforms to the Principle of Corresponding States,[20] with an addition parameter, the acentric factor, ω, which allows for the deviation of the molecule from spherical symmetry. This factor is defined empirically by[19]

$$\omega = -\log\left(\frac{P_s}{P_c}\right) - 1.00 \tag{22}$$

where

$$P_s = \text{vapour pressure at } T_s = 0.7T_c$$

On this definition $\omega = 0$ for simple fluids (typically the heavier inert gases) and is positive for all other fluids. Among the other fluids the criterion for "normality" used by Pitzer is defined in terms of the gas-liquid interfacial tension of the substance. A large number of substances conform to the empirical rule

$$v_0^{2/3}\gamma_0 T_c^{-1} = 1.86 + 1.18\omega \text{ erg } K^{-1} \text{ mol.}^{-2/3} \tag{23}$$

where v_0 and γ_0 are the constants in the equations[20]

$$v_m = v_0\left(\frac{T_c - T}{T_c}\right)^{-1/3} \tag{24}$$

$$\gamma = \gamma_0\left(\frac{T_c - T}{T_c}\right)^{11/9} \tag{25}$$

which fairly accurately express the temperature dependence of v_m and γ for most liquids, whether normal or not, for $T < 0.85T_c$. "Normality" is defined as conformity with Eq. (23) to within 5%. Most liquids which are not hydrogen bonded or highly polar are "normal" on this definition. Some examples are shown in Figure 5. For hydrogen bonded liquids the value of $v_0^{2/3}\gamma_0 T_c^{-1}$ is much lower than that given by Eq. (23).

The thermodynamic surface excess properties of normal liquids can conveniently be expressed in terms of the quantity $v_0^{2/3}\gamma_0 T_c^{-1}$. For brevity we will define

$$\Omega = \left(\frac{v_0}{N_A}\right)^{2/3} \gamma_0 T_c^{-1} \tag{26}$$

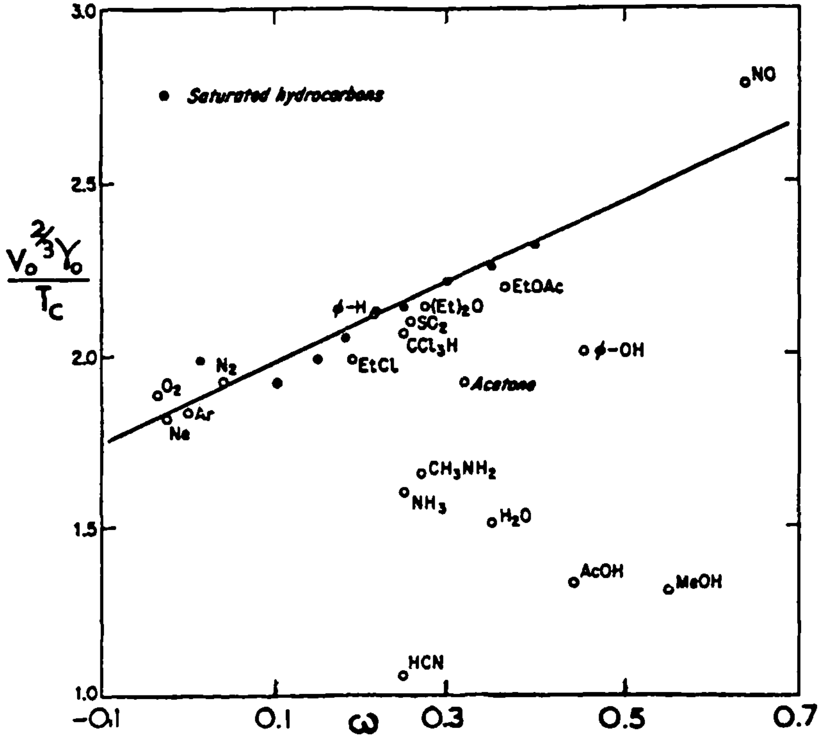

FIGURE 5 Relation between $v_0^{2/3}\gamma_0 T_c^{-1}$ and ω for several liquids. The line represents Eq. (23), and a fluid is "normal" if $v_0^{2/3}\gamma T_c^{-1}$ lies within ±5% of this line. After R. F. Curl Jr. and K. S. Pitzer, *Ind. Eng. Chem.*, 50, 265 (1958).

then using Eqs. (24) and (25) with Eqs. (18) to (21), we obtain

$$a\gamma = \Omega\,(T_c - T) \tag{27}$$

$$s^{\sigma e} = (\tfrac{11}{9})\,\Omega \tag{28}$$

$$u^{\sigma e} = \Omega\,(T_c + \tfrac{2}{9}T) \tag{29}$$

Benzene is an example of a "normal" fluid for which $\omega = 0.22$. Figure 6a shows that the calculated and experimental quantities (Δuev. is calculated with the aid of Table I of Ref. 19) are in good agreement up to 473 K ($0.85T_c$). Since Eq. (24) is an approximation valid only when v_m (vapour) $\gg v_m$ (liquid), it must fail as T approaches T_c. The surface excess entropy is remarkably independent of temperature as has been pointed out by Harkins and Roberts[21] and by Eriksson[15b], and as is required by Eq. (28).

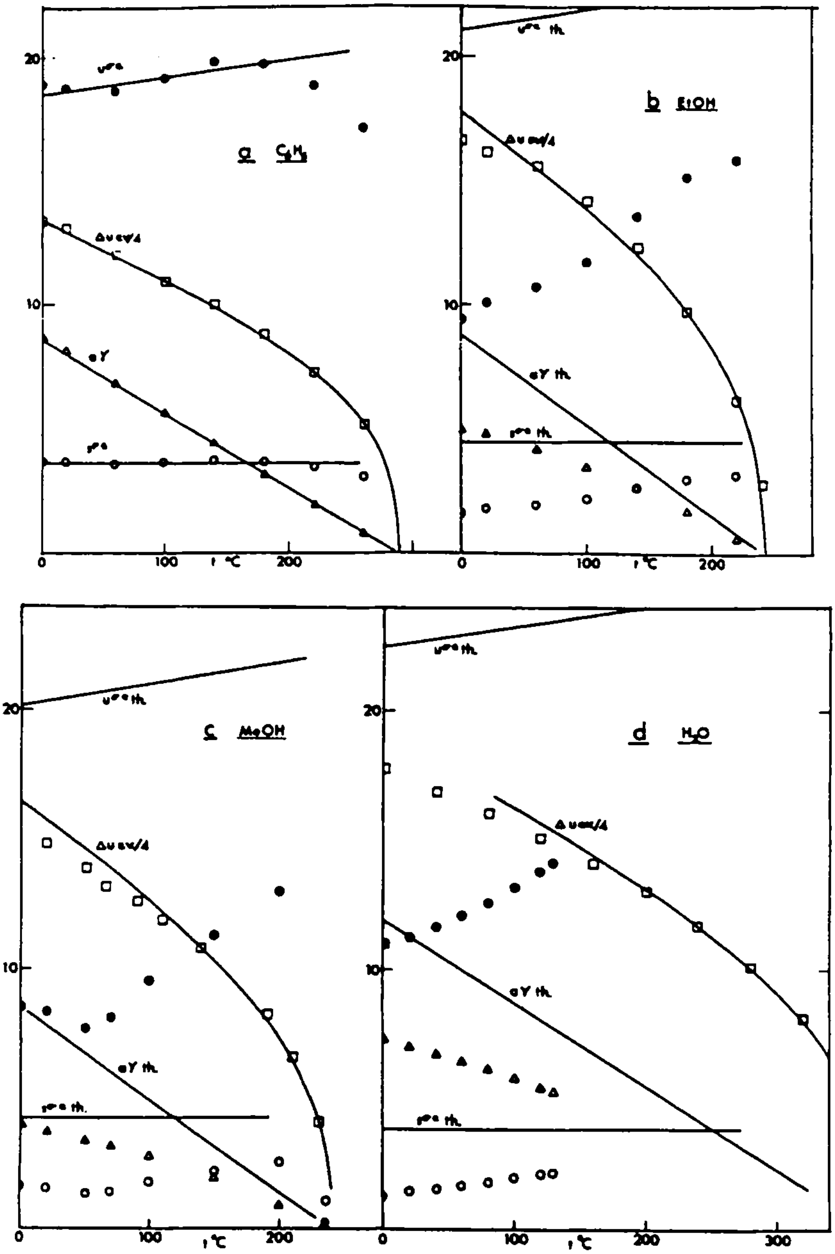

FIGURE 6a, b, c, d Experimental points: ○ molecular surface excess entropy, $s^{\sigma e}$; △ molecular surface energy, $u^{\sigma e}$; ⊖ molecular surface excess free energy, $a\gamma$; □ molecular energy of evaporation/4. Lines are calculated from equations 26–29 for a normal fluid having the same value of ω: i.e. $\omega = 0.22$ (C_6H_6), 0.64 (EtOH), 0.56 (MeOH), 0.35 (H_2O). Δu ev is calculated with the aid of Table 1 of Ref. 19. Units of ordinates: 10^{-16} erg K^{-1} molecule^{-1} for $s^{\sigma e}$ and 10^{-14} erg molecule^{-1} for $u^{\sigma e}$, $a\gamma$ and Δuev/4.

For ethanol ω is 0.64, for methanol 0.56 and for water 0.35. The values of Δuev. (calculated as for benzene) are in reasonable agreement with the measured values (Figures 6b, c and d). The values of surface properties calculated from Eq. (27) to (29) are, however, in gross disagreement with experiment. For ethanol at 310 K ($= 0.6T_c$) $u^{\sigma e}$ is less than half the calculated value and is actually about equal to that calculated for ethane at the same reduced temperature. It is therefore a plausible hypothesis that the ethanol molecules at the surface are oriented with the $—C_2H_5$ directed to the vapour phase so that the formation of new surface does not require the breaking of hydrogen bonds. Correspondingly $s^{\sigma e}$ is about half what it would be for a normal liquid of the same ω.

An important question about the surface of water is whether or not there is a considerable degree of preferred orientation of water molecules in the surface zone. The low surface excess entropy (Figure 6d) may be regarded as evidence that there is. However, a comparison of $s^{\sigma e}$ (theoretical) $-$ $s^{\sigma e}$ (experimental) for EtOH, MeOH and H_2O all at the same reduced temperature ($T = 0.6T_c$) shows that the deficit is least for water.

TABLE I

	EtOH	MeOH	H_2O	H_2O
$T =$	310	308	388	(310)
$\dfrac{s^{\sigma e}(\mathrm{Th}) - s^{\sigma e}(\mathrm{Exp.})}{10^{-16}\mathrm{erg\,K^{-1}mol^{-1}}} =$	2.7	2.6	1.8	2.3

For water, even at the same absolute temperature (310 K) as the other two liquids, the deficit is still smaller than for them. Another point worth noting is that while $s^{\sigma e}$ for water is low, the entropy of the liquid itself is also unusually low. Thus at $T = 0.6T_c$, $s^{\sigma e}/s_{\mathrm{liq}} = 0.14$ for water compared with 0.078 for methanol.

Water is a highly structured liquid and evidently much of this structure is retained up to the surface. However, the evidence points to water having less additional structure at the surface than do methanol and ethanol. This is in agreement with the conclusions about the surface potential of water reached in Section 4.2 of this Report. It is also evident from Figure 6 that with increasing temperature both $u^{\sigma e}$ and $s^{\sigma e}$ for the abnormal liquids approach towards the values they would have if the liquids were normal. This conforms to the expectation that the degree of additional structure in the surface declines with increasing temperature, and is in agreement with the temperature dependence of the surface potential also discussed in Section 4.2.

1.3 "Anomalies" in the Temperature Dependence of the Surface Tension of Water

Although in the preceding section the change of surface tension of water with temperature has been tacitly assumed to follow a smooth curve, we cannot ignore entirely the argument about "anomalies" which has continued for some years, since these anomalies are supposed to have a structural origin. The arguments in favour of "kinks" in the surface tension-temperature curve and in the temperature dependence of other properties have been summarised by Drost-Hansen.[1a,b] The evidence in favour of such anomalies has been criticised frequently in recent years. Falk and Kell[22] concluded that the "kinks" in the temperature dependence of the vibrational spectrum, the volume and the compressibility of water were all artefacts or within experimental error. They remark that "the balance of evidence is that the physical properties of water do vary continuously with temperature." Similar conclusions were reached by Rusche and Good[23] and were also expressed by R. L. Kay.[24]

With regard to surface tension in particular Claussen[25] concluded that the data existing in 1967 were compatible with a "smooth linear plot" of the function $\gamma v_m^{2/3}$ against temperature. A very careful study by G. J. Gittens[26] specifically aimed at assessing the reality or otherwise of the surface tension anomalies, concluded (while cautiously suggesting that further work would be useful) that the present evidence pointed to "the absence of significant kinks in the variation of the surface tension of pure water with temperature." Taking the trend of evidence and opinions into account I think we must accept that the unusual properties of water as a liquid do not include "kinks" in the temperature dependence of its surface tension.

1.4 Kinetic Behaviour of the Gas-Liquid Interface of Water

The equilibrium data which we have used so far in discussing the surface structure of water may be supplemented to some extent by kinetic measurements, in particular of the exchange of molecules between vapour and liquid. If there is a well developed surface structure it can be expected that a molecule from the vapour phase colliding with the liquid surface will "bounce," i.e. reflect, rather than be incorporated in the liquid, if its orientation is not within a narrow range of solid angle compatible with the surface structure at the point of collision. This possibility is expressed quantitatively by the "condensation coefficient," κ, which equals the fraction of vapour phase molecules striking the liquid surface which actually condense. If the vapour is "dilute" the number of molecules striking unit area of liquid surface per second can be calculated from the kinetic theory of gases, and at equilibrium this is equal to the number evaporating from unit area per second. By increasing or decreasing the vapour pressure net condensation or evaporation is caused. From the rate of condensation or evaporation κ can be calculated provided that the temperature of the water surface is held constant, or at least is known. Many years ago Alty[27] measured the rate of evaporation of water droplets into a vacuum and concluded that $\kappa = 0.04$, whereas for non-polar liquids it was usually unity. A similar low value of κ for water and other hydrogen bonded liquids has been obtained by other workers.[28] However, these results, and in particular the work of Alty, have been criticised by Hickman.[29] Alty estimated the surface temperature of his water drops, which were formed at the end of a capillary tube, from the surface tension which was calculated from the size of drops when they fell. In Hickman's view the surface temperature was lower than that calculated by Alty and in general Hickman concluded that "heat starvation of the surface layers is the cause of low measured evaporation rates." This may be true; the experiments in which low evaporation or condensation rates were found have used static surfaces and incorrectly estimated or measured surface temperatures may have been common. More recent experimental work[30] appears to show that evaporation or condensation coefficients of near unity can be obtained for the surface of a high speed jet of water immediately after its emergence from an orifice. This is explained on the grounds that the jet method avoids contamination of the surface and minimises errors in the surface temperature (the exposure of the jet is so brief that the surface temperature changes very little) both of which are faults of the static surface methods. On the other hand it may be argued that either (a) the short life, or (b) the turbulence, of the surface of the jet, prevents the formation of a normally structured water surface. The life of the surface while exposed to evaporation or condensation was [30] about 10^{-3} sec. The dielectric relaxation time of water is about 10^{-11} sec., and it is difficult to see how even co-operatively structured regions could have a lifetime greater than 10^{-6} sec. It seems more possible that turbulence may prevent the formation of the normal surface structure on the jet. Two facts argue against this, however. Surface potential measurements indicate no dissymmetry between a jet of a dilute aqueous electrolyte solution and a stationary or slowly moving surface of the same solution (Section 3.2). Secondly, the most recent measurements do not support the view that water has a dynamic surface tension different from the static one. Measurements by the oscillating jet method appeared to show[31] that the surface tension of a freshly emerged surface of water was significantly higher than that of a static surface, for a period of 10–20 millisec from emergence. However, there seems to be good evidence[32] that the discrepancy was due to the real hydrodynamic situation in the jet being different from that supposed in the theory of the method. If the surface tension is in fact equal to the static value, from the smallest time that could be measured (~ 1 msec.), then the surface structure is probably normal and the high κ values obtained with a jet are probably valid. Obviously the matter cannot be regarded as settled, but to the extent that we can accept the validity of the high value of κ, so we can deduce that the surface of water is not highly organised.

2 THE SURFACE TENSION OF AQUEOUS ELECTROLYTE SOLUTIONS

2.1 Basic Thermodynamics

The surface tension of aqueous solutions of most simple inorganic salts is greater than that of pure water and therefore such salts are in general negatively adsorbed, i.e. repelled from the surface. The quantitative relationship is the Gibbs adsorption equation. The Gibbs–Duhem equation for phase σ is obtained by differentiating Eq. (10) and subtracting from (12). At constant temperature the result is

$$0 = V^\sigma \, \mathrm{d}P - A \, \mathrm{d}\gamma - \sum_i N_i^\sigma \, \mathrm{d}\mu_i \tag{30}$$

The Gibbs–Duhem equation for phase α also at constant temperature is

$$0 = V^\alpha \, \mathrm{d}P - \sum_i N_i^\alpha \, \mathrm{d}\mu_i \tag{31}$$

If the composition is changed at constant temperature the change of vapour pressure ($\mathrm{d}P$) is not in general zero. However, if we choose α to be the *liquid phase* $V^\alpha \, \mathrm{d}P$ in (31) and also $V^\sigma \, \mathrm{d}P$ in (30) can be neglected. Then, if we name the solvent as component 1, $\mathrm{d}\mu_i$ can be eliminated from (30) by use of (31) to give

$$-A \, \mathrm{d}\gamma = \sum_{i=2}^{\infty} \left(N_i^\sigma - \frac{N_i^\alpha}{N_1^\alpha} . N_1^\sigma \right) \mathrm{d}\mu_i$$

or

$$-\mathrm{d}\gamma = \sum_{i=2}^{\infty} \Gamma_{i(1)} \, \mathrm{d}\mu_i \tag{32}$$

For our purpose it is sufficient to consider solutions of a single salt (component 2) in water for which (32) becomes

$$\frac{-\mathrm{d}\gamma}{\mathrm{d}\mu_2} = \frac{1}{A} \left(N_2^\sigma - \frac{N_2^\alpha}{N_1^\alpha} . N_1^\sigma \right) = \Gamma_{2(1)} \tag{33}$$

The quantity $\Gamma_{2(1)}$ is the surface excess of solute (2) relative to solvent (1) with the bulk liquid as the reference phase. It is easily seen that the converse form of (33) defines the surface excess of the solvent relative to the solute,

$$-\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_1} = \Gamma_{1(2)} = -\frac{N_1^\alpha}{N_2^\alpha}.\Gamma_{2(1)} \tag{34}$$

2.2 Temperature dependence

The temperature dependence of the surface tension of a solution, at constant composition, yields the surface excess entropy (compare Eq. (19) for the pure solvent). Early measurements[33] show that $\mathrm{d}\gamma/\mathrm{d}T$ for aqueous solutions of most simple inorganic salts is equal or almost equal to that of pure water. Since most salts are desorbed this is not surprising and it is unlikely that much information would be gained from such measurements on dilute solutions. There has recently been some interest in the structure of very concentrated electrolyte solutions, and it seems possible that studies of the temperature dependence of the surface tension of these solutions might lead to useful information. No work of this sort seems to have been done, however.

2.3 Concentration dependence

The electrolytes with which I am concerned in this report are primarily simple inorganic salts and acids, with some reference to tetra-alkyl ammonium ions; that is with those electrolytes which have been the subject of most studies of the bulk structure of electrolyte solutions. I shall exclude strongly surfactant electrolytes (e.g. long chain cations or anions, or "soaps") whose surface and bulk behaviour (e.g. micelle formation) lie outside the scope of the Report.

For the simple inorganic electrolytes early studies[34] showed that in very dilute solutions equivalent concentrations of electrolytes of the same valence type gave similar surface tension increments ($\Delta\gamma$) while at higher concentrations specific differences appeared. The situation is therefore similar to that which exists in the interpretation of the bulk properties of electrolyte solutions. In dilute solutions the emphasis must be on the "primitive model" in which ions are treated as charged particles or rigid spheres in a structureless dielectric medium.[35] At higher concentrations, as the regions of strong polarisation of the dielectric by ions begin to overlap with each other, or with the phase boundary, the molecular structure of the dielectric must be taken into account if the model is to be realistic. Unfortunately because of the complexity of the interactions of water molecules with each other the theoretical interpretation of such concentrated solutions inevitably becomes largely qualitative.

The first theory of the surface tension of dilute aqueous solutions of electrolytes was due to Wagner[36] and followed the principles established by Debye and Huckel. A particle of charge e in a medium of dielectric constant ε, at a distance x from a plane boundary with a medium of dielectric constant ~ 1, is repelled from this boundary by an image force equal to $e^2(\varepsilon - 1)/4x^2\varepsilon(\varepsilon + 1)$. Since for water $\varepsilon \gg 1$, the force may be taken as $e^2/4x^2\varepsilon$. If it is assumed that all ions approaching the free surface of an aqueous electrolyte solution are subject to this repulsive force and a Boltzman distribution is worked out on this basis it is found that the surface deficit of ions becomes infinite. This paradoxical situation results from the omission of the screening effect of the ionic atmosphere. When x becomes larger than the Debye length $1/\kappa$ the image force of the ionic atmosphere largely cancels that of the central ion. The surface deficit should therefore be deduced from a Boltzman distribution which has been calculated with screening by the ionic atmosphere taken into account. Because the ionic concentration and hence the value of κ change as the surface is approached an exact mathematical solution is difficult. Wagner only obtained solutions requiring laborious numerical integration but further simplifying approximations were made by Onsager and Samaras[37] who, using Eq. (33), were able to tabulate values of the theoretical surface tension increment. They also derived a limiting law for low concentrations of 1–1 electrolytes, which for aqueous solutions at 298 K takes the form

$$\Delta\gamma = \gamma - \gamma_0 = 1.012\ \mathrm{m}\log_{10}(1.467/\mathrm{m})\ \mathrm{erg\ cm^{-2}} \qquad (35)$$

where m = mol. solute/kgm water.

In order to test the validity of Eq. (35) and of other results of Onsager and Samaras, accurate measurements of the surface tension of very dilute electrolyte solutions were required. Experiments designed to provide these were undertaken by Jones and Ray[38] using a very sensitive differential capillary rise method with silica capillaries. Unfortunately this method produced a "red herring" in the form of an anomalous initial decrease in surface tension with increasing concentration in the range 0 to 10^{-3} M followed by the usual increase (see Figure 7). The phenomenon became known as the Jones–Ray effect and efforts were made[39] to explain it as a true surface tension change. However, it was suggested by Longmuir[40] that it was an artefact caused by a variation of the thickness of the "wetting layer" on the inside of the very fine silica capillaries which occurs when the solutions are very dilute. This changes the effective diameter of the capillary and produces a misleading change in the capillary rise. It is unnecessary to go into details, but since the Jones–Ray effect is still referred to occasionally[41] as an example of the supposedly anomalous behaviour of aqueous solutions it is worth while mentioning the evidence that it is an artefact. (1) Jones and Wood[42] calculated

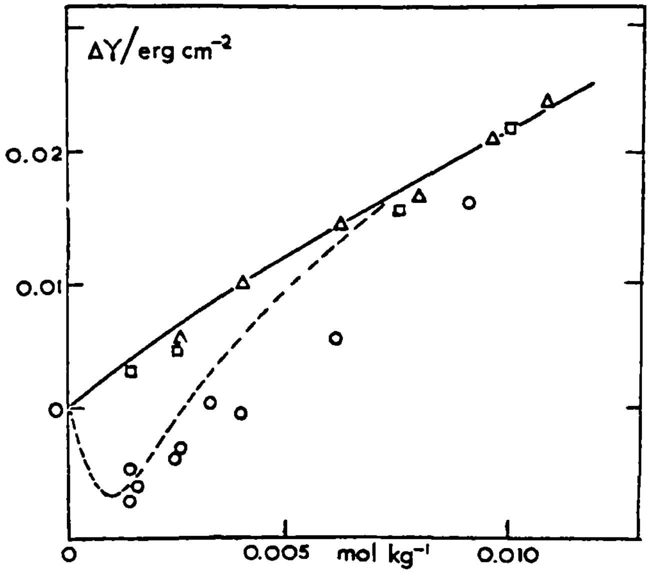

FIGURE 7 Broken line: Jones and Ray[38] experimental Δγ for NaCl in water; full line, Onsager-Samaras equation.[47] Experimental points Passoth,[44] △ NaCl, □ KBr with bubble interval 15 sec., ○ NaCl with bubble interval 120 secs.

the correction to be applied to the measured capillary rise of very dilute KCl solutions to take account of the change in effective radius of the capillary. When the corrections were applied the apparent initial decrease in γ vanished. Similar calculations by Robinson[43] led to the same conclusion. (2) Passoth[44] showed that a maximum bubble pressure method for measuring γ could either give, or fail to give, a Jones–Ray effect. This depended on the time interval between bubbles, which determined whether the thickness of the wetting layer varied with solution concentration, or was independent of it. Some of Passoth's results as shown in Figure 7. (3) Measurements of the surface tension of 1–1 electrolytes using the horizontal wire-detachment method differentially[45] failed to show any Jones–Ray effect. This is because any change in the thickness of the solution film adhering to the wire will not affect the measured force of detachment from the liquid surface. A more detailed discussion of these arguments has been given elsewhere.[46]

When the Jones–Ray effect has been eliminated the slope of the γ vs. concentration curve for low concentrations of non-surface-active 1–1 electrolytes is in good agreement with that calculated by the Onsager–Samaras equation (see Figure 7). However, the theoretical curve falls well below the experimental curves at concentrations above about 10^{-2} M (Figure 8). The deficiencies of the model employed in the Onsager–Samaras theory are: (1) it

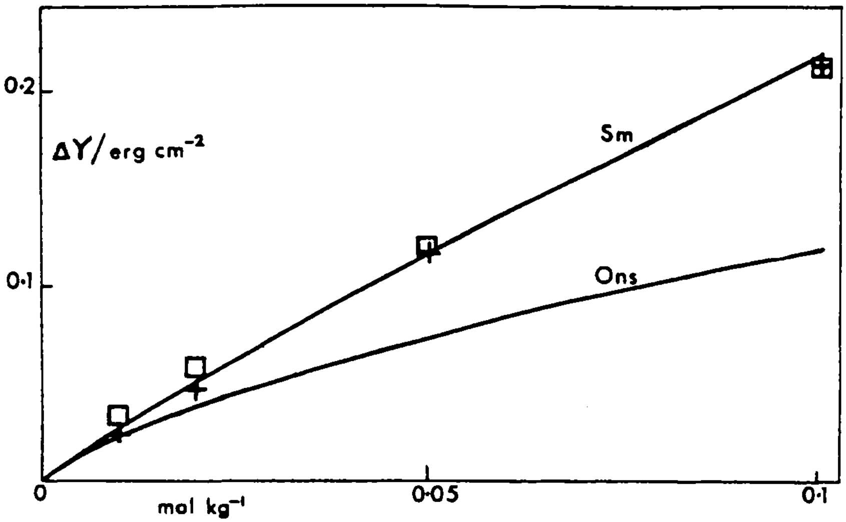

FIGURE 8 Experimental points: ☐ NaCl, + KCl, from Jones and Ray.[38] Lines: Ons – Onsager and Samaras[37] calculated values; Sm–Schmutzer's[49] Eq. (36) with δ = 3.2Å.

ignores the change in the radius of the ionic atmosphere as the surface is approached; (2) it treats the change of dielectric properties at the surface as occurring abruptly at a geometric plane; (3) it ignores the strong interactions between some ions and their nearest neighbour water molecules. The first deficiency is of a kind which a more sophisticated calculation still based on the "primitive model" could overcome. Buff and Stillinger[47] using a pair distribution function for the calculation of the coulombic energy have extended the range of agreement between theory and experiment but not beyond about 0.02 M.

The only theories which are able to produce results in agreement with experiment at concentrations up to 1 M or more are those which take account of the firmly held first hydration shells of ions. Schäfer *et al.*[45] interpreted the image force repulsion of ions from the surface as due to a loss of (negative) hydration energy as an ion approached the surface. Specific behaviour of different ions of the same charge was introduced by using Webb's values of "effective" ionic radii and of the dielectric constant of water close to an ion. However, agreement with experiment was only obtained after adjusting Webb's dielectric constants and using an arbitrary distance of closest approach to the surface. In an approximately simultaneous publication Schmutzer[49] used a rather simpler approach. He assumed a layer of arbitrarily chosen thickness, δ, at the upper limit of the liquid phase to be ion-free (ions being excluded by an infinite potential barrier). He calculated the ion distribution below this layer by a method similar to that of Onsager and Samaras. The formula he obtained was

$$\Delta\gamma = \gamma - \gamma_0 = \frac{N_A kT\delta}{1000}.vm\phi + \frac{kT}{32\pi\delta^2}\bar{I}_0(2\delta\kappa) \tag{36}$$

where m is mole solute/Kgm solvent, v the number of ions produced by one molecule of solute, k is the Boltzmann constant, ϕ the molal osmotic coefficient of the solution and κ the reciprocal of the radius of the ionic atmosphere. The function $\bar{I}_0$ is an integral, and its value for a range of values of $(2\delta\kappa)$ is tabulated by Schmutzer.[49] The second term on the right hand side of Eq.(36) represents the surface tension increment due to the deficit of ions beyond the ion-free layer of thickness δ. The first term represents that due to the ion-free layer itself, as will now be shown. If the molar volume of the solvent (water) is v_1, then an ion-free layer of thickness δ represents a surface excess of $N_A\delta/v_1$ molecules of water per unit area. Hence Eq. (34) for the change of γ due to the ion-free layer becomes

$$-\frac{d\gamma}{d\mu_1} = \frac{N_A\delta}{v_1} \tag{37}$$

The molal osmotic coefficient of an aqueous solution is related[50] to $ln a_1$ by

$$ln a_1 = \frac{-18}{1000} vm\phi = \frac{-v_1}{1000} vm\phi \tag{38}$$

(taking the density of water to be 1 gm cm^{-3}). Hence

$$d\gamma = \frac{N_A kT\delta}{1000} d(vm\phi) \tag{39}$$

which, if δ is assumed to be constant integrates to the first term on the right hand side of Eq. (36).

At very low concentrations the first term on the right of Eq. (36) becomes negligible in comparison with the second and the limiting law from Schmutzer's equation is identical with that of Onsager and Samaras. Physically this is because at low concentration the surface zone is free from ions because of the image force repulsion and the assumption of an ion-free layer makes no difference. At higher concentrations Schmutzer's equation with an appropriately chosen value of δ predicts surface tension increments in good agreement with the experimental values for 1-1 surface-inactive electrolytes. The curve calculated with δ = 3.2 Å is included in Figure 8. The agreement of Schmutzer's equation with experiment is as good as that obtained by Schäfer,

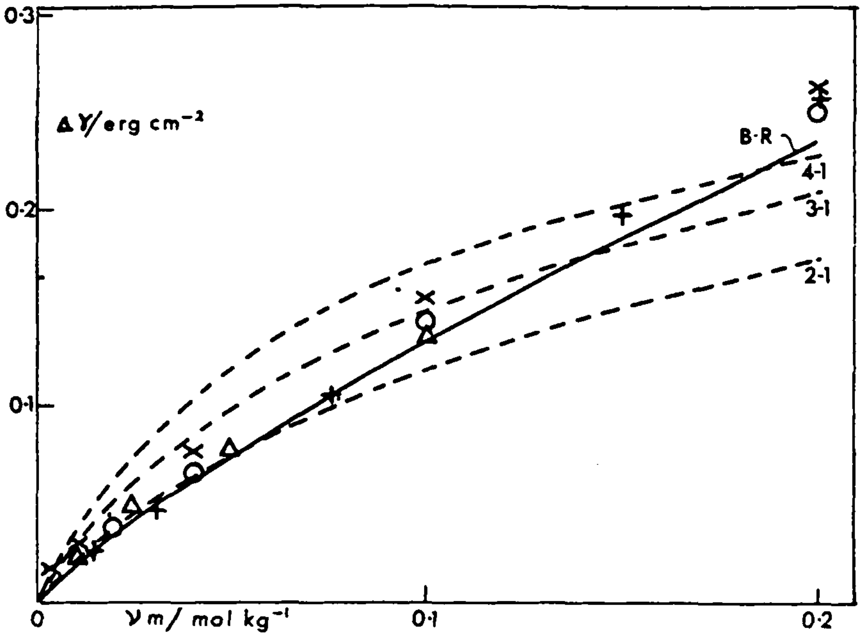

FIGURE 9 $\Delta\gamma$ for higher valency electrolytes in water. Experimental points: + $BaCl_2$. ○ $LaCl_3$, × $MgSO_4$. □ $K_4Fe(CN)_6$. Broken lines, limiting law Eq. (40) (the line for a 2–2 electrolyte coincides with that for 4–1). Full line, Bell and Rangecroft[51] calculated values for a 2–1 electrolyte.

Perez-Masia and Jüntgen. In view of the uncertainties in the latters' use of Webb's data, it is doubtful whether their theory represents any more fundamental interpretation of the repulsion of ions from the surface than does Schmutzer's avowedly arbitrary ion-free layer.

So far only electrolytes of 1–1 valence type have been considered. For higher valence electrolytes Schmutzer gives the equation

$$\Delta\gamma = 0.506\,m\,\Sigma\,\nu_i\,z_i^2\,\log_{10}(2.934/m\,\Sigma\,\nu_i\,z_i^2)\ \text{erg cm}^{-2} \qquad (40)$$

Eq. (35) is the special case of this equation for a 1–1 electrolyte. A comparison of $\Delta\gamma$ calculated by Eq. (40) with some experimental results is shown in Figure 9. As expected the calculated value falls below the experimental value as the concentration rises. An improved calculation, still based on the "primitive model," for a 2–1 electrolyte has been carried out by Bell and Rangecroft[51] which, as shown in Figure 9, gives better agreement than does the limiting law†. It also falls increasingly below the experimental values

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† Note that the limiting law curve shown in Ref. 51 Figure 2 is incorrect and exaggerates its deviation from the experimental values.

with increase of concentration as apparently must any theory which does not incorporate the molecular character of the dielectric and of the hydration shells of the ions in particular. For 3–1 and higher valence electrolytes Eq. (40) overestimates $\Delta\gamma$ at low concentrations while still falling below experimental values at high concentrations. Ion pairing, and in some cases hydrolysis, makes the significance of the experimental values uncertain for these solutions.

In general it appears that the surface tension of aqueous solutions of non-adsorbed electrolytes at moderate to high concentrations can only be accounted for on the basis of there being an ion-free layer at the surface. In Eq. (36), the first term on the right hand side (the ion-free layer term), when $\delta = 3.2$ Å is about twice the second term for a 0.1 M solution of a non-adsorbed 1–1 electrolyte, and about 6 times the second term for a 1.0 M solution. Hence at concentrations of 0.5 M upwards we shall not be far wrong if we interpret the whole surface excess of solvent ($\Gamma_{1(2)}$) as due to an ion-free layer. It is therefore of interest to calculate $\Gamma_{1(2)}$ and express it as equivalent monolayers of water. We will take the number of molecules of water in unit area of a monolayer to be $(N_A/v_1)^{2/3}$ (compare Eq. 18); then $\Gamma_{1(2)}$ is equivalent to y monolayers if

$$y = \Gamma_{1(2)}\left(\frac{v_1}{N_A}\right)^{2/3} = -\left(\frac{v_1}{N_A}\right)^{2/3}\frac{\mathrm{d}\gamma}{\mathrm{d}\mu_1}$$

Using Eq. (38) and inserting numerical values this becomes

$$y = 1.30\frac{\mathrm{d}\gamma}{\mathrm{d}(vm\phi)} \tag{41}$$

at 298 K and with γ in ergs cm^{-2}. Some graphs at $\Delta\gamma$ against $(vm\phi)$ are shown in Figures 10 and 11.

Most of the curves in Figures 10 and 11 have a constant or slowly decreasing slope in the range $vm\phi > 1$ indicating a fairly constant value of y. Values of y are tabulated in Table II.

TABLE II

Values of y for several salts

$vm\phi$/mol kgm^{-1}	NaCl, KF, KCl	KI	$KClO_3$	KCNS
1.0	1.10	0.6	0.54	0.28
2.0	1.05	0.57		0.28
4.0	1.00	0.55		0.31

$vm\phi$/mol kgm^{-1}	K_2SO_4	$BaCl_2$	$MgSO_4$	$LaCl_3$	$K_4Fe(CN)_6$	$Al_2(SO_4)_3$
1.0	1.65	1.49	2.3	1.77	2.05	2.25
2.0		1.33	2.0	1.34		2.0
4.0				0.93		2.1

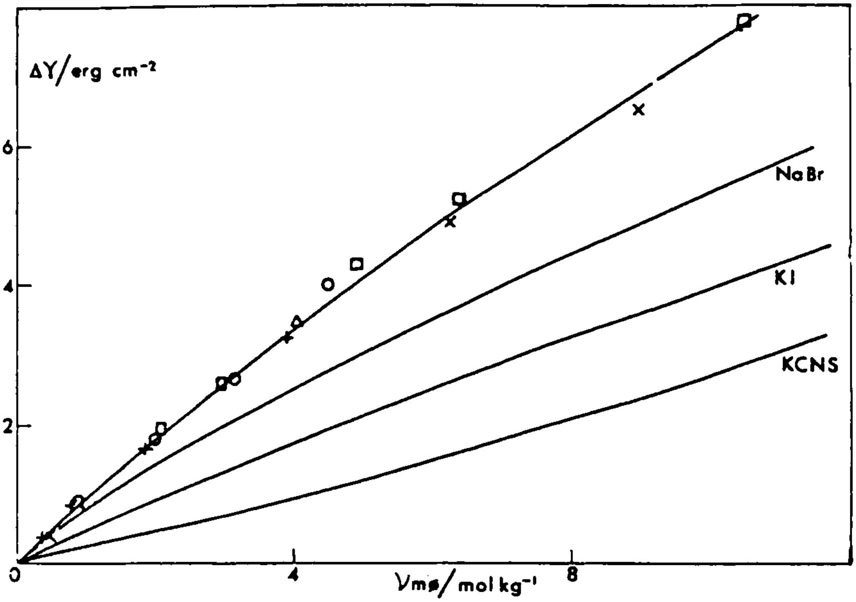

FIGURE 10 Δγ plotted against $\nu m\phi$ for several electrolytes in water. The slope is proportional to the surface excess of water. The uppermost line is common to the non-surface active electrolytes; + KCl, △ NaCl, (data from Ref. 38); × NaCl, ○ KOH (from Ref. 33); □ KF (from Ref. 34).

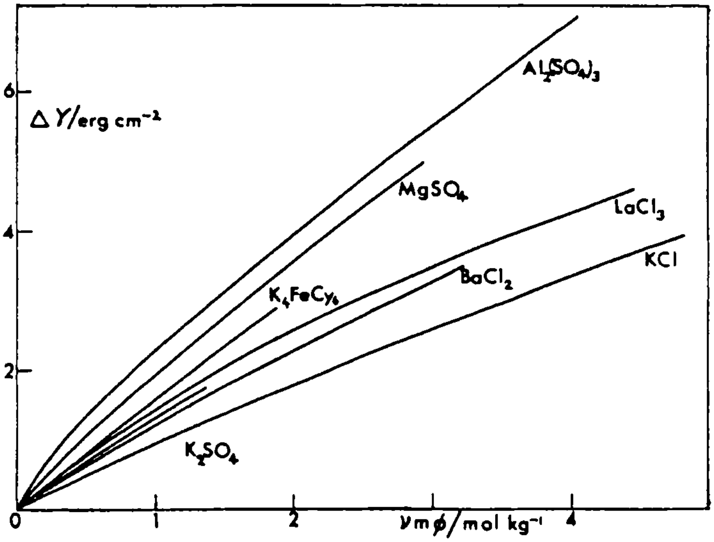

FIGURE 11 Δγ plotted against $\nu m\phi$ for higher valency electrolytes.

Surface potential measurements (Section 3.3) show that the ions Na^+, K^+, F^-, Cl^- are all repelled from the surface to approximately the same extent. Hence the fact that $y \simeq 1$ for the salts NaCl, KF and KCl in Table II can be interpreted as meaning that each of these ions as it approaches the surface retains at least one water molecule between itself and the gas phase, thus leaving one monolayer of water free from ions. While these monovalent ions retain their first layer hydration shell as they approach the surface the decreasing values of y for the salts KI, $KClO_3$, KCNS indicate an increasing ease of loss of this shell by the anions of these salts. The salt KPF_6 is actually adsorbed indicating that despite the electrostatic image force repulsion which must still operate for PF_6^- ion, there are other specific adsorptive forces operating on PF_6^- sufficiently strong to give a net surface excess of both ions.

From the values of y for the salts $BaCl_2$, $SrCl_2$, Na_2SO_4 and $MgSO_4$ we can deduce that the divalent ions in these salts retain a two layer hydration shell when they approach the surface. In solutions of $CaCl_2$ at high concentration y falls to lower values because of shortage of water, e.g. in a 7 M solution ($vm\phi = 60$) there are fewer than 8 water molecules for each group of $Ca^{2+} + 2Cl^-$ ions, and $y = 0.32$.

2.4 Tetra-alkyl Ammonium Ions

The behaviour of tetra-alkyl ammonium salts in solution has recently been studied by many investigators, in relation to the capacity of the cations to influence the structure of water adjacent to them.[52] Surface tension data are meagre, however. The measurements of Rehbinder[53] are plotted in Figure 12 with $\Delta\gamma$ of KCl and KPF_6 for comparison. Obviously tetra-alkyl ammonium cations are subject to adsorptive forces increasing with increasing size of the alkyl groups. Further discussion of the behaviour of these ions and of the inorganic anions will be deferred until we have considered the implications of surface potential measurements.

2.5 Aqueous solutions of Inorganic Acids

No mention has so far been made of solutions of acids. In general the simple inorganic acids raise the surface tension of water less, or lower it more, than do the corresponding alkali metal salts, see Figure 13. The behaviour of HCl is unusual; it raises the surface tension of water at very low concentrations and lowers it at higher concentrations.[54,55] The probability is that molecular HCl is surface active. Since $a_{HCl} \propto a_{\pm}^2$, at low concentration the activity of molecular HCl is so small that no significant amount can appear even in the surface layer, and the net desorption of $H^+ + Cl^-$ leads to a rise in surface tension. At higher concentrations molecular HCl appears in the surface layer

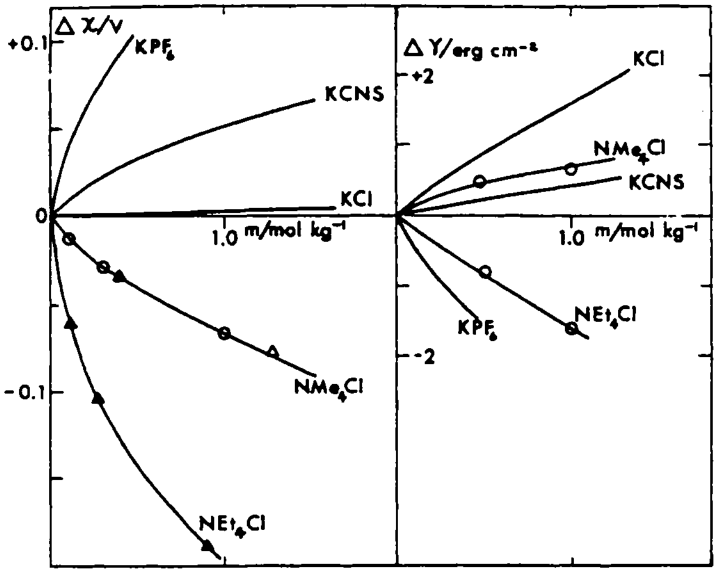

FIGURE 12 Surface potential increments, Δχ, and Δγ for some tetra-alkyl ammonium salts and other 1–1 electrolytes, plotted against molality. Surface potentials: △ from Ref. 60, ○ from Ref. 69. Surface tensions: ○ from Ref. 53.

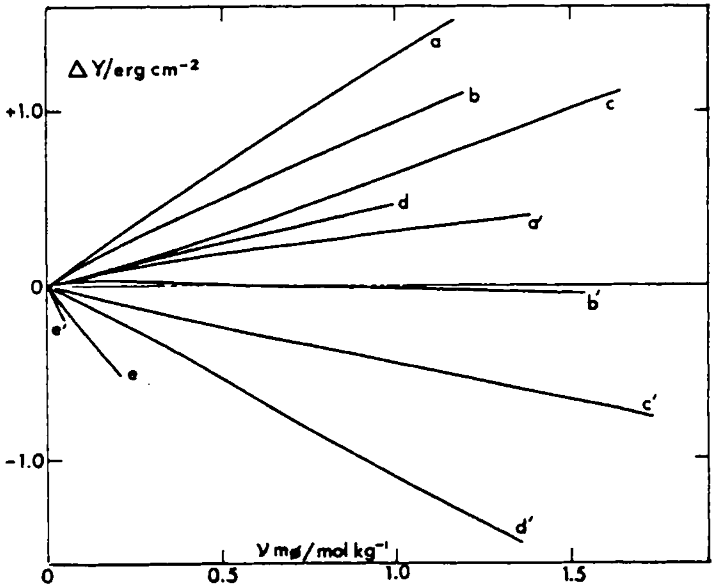

FIGURE 13 Δγ of some salts and acids: *a* and *a'*, K_2SO_4 and H_2SO_4; *b* and *b'*, KCl and HCl; *c* and *c'*, KNO_3 and HNO_3; *d* and *d'*, $KClO_3$ and $HClO_4$; *e* and *e'*, KPF_6 and HPF_6.

sufficient to give a net surface excess of acid and a decrease of surface tension, even though the bulk concentration of molecular HCl is very small. The acids HNO_3, $HClO_4$ and HPF_6 are all stronger acids than HCl, as also is H_2SO_4 in its first dissociation, and they show no similar change of slope. If we compare the surface tension curves of the acids with those of the K^+ or Na^+ salts (using the low concentration region for HCl) we see that in all cases the acids are less desorbed or more adsorbed than are the salts. The difference may be expressed as difference between y for salt and y for acid at equivalent concentrations (when the solute is adsorbed, y is negative). The differences are: for $HClO_3/KClO_3$ and HPF_6/KPF_6, $\Delta y = 1.7$; H_2SO_4/K_2SO_4 and HNO_3/KNO_3, $\Delta y = 1.4$; HCl/KCl, $\Delta y = 1.0$. No great significance should be attached to the actual figures but in all cases the surface excess of water is considerably greater for the salts, clearly indicating that hydrogen ion is more surface active than potassium ion. The magnitude of the difference seems to imply that hydrogen ion is not inhibited, as are the alkali cations, from entering the uppermost layer of molecules of the liquid-gas transition zone, and may even be attracted into it. If this is accepted, however, the effect of acids on the surface potential of water is anomalous and requires special explanation as will be discussed in Section 3.3.

3 THE SURFACE POTENTIAL OF AQUEOUS ELECTROLYTE SOLUTIONS

3.1 Introduction

The definition of the electrical potential of condensed phases and of the difference of potential across phase boundaries has always been a source of discussion. The subject was excellently reviewed some years ago by Parsons[56] and there is a recent article on the subject of surface potentials and methods of measuring them by Llopis.[57] Only a summary of the nature of surface potentials and methods of measurement will be given here.

The surface potential of a liquid or solid is the difference of electrical potential across the interface between the phase and a vacuum or a gas at low density. Surface potentials obviously depend on the composition and structure of the transition zone between the condensed phase and the gas phase, and for a solid it is very difficult to control this or ensure its uniformity. For a liquid the situation is better but traces of a strongly surface active substance can grossly affect surface potentials as they can surface tension. In experimental work the accidental presence of such substances must be avoided. The surface potential between a liquid and a gas is normally independent of the composition of the gas phase if this is of low density, inert and not strongly adsorbed by, or soluble in, the liquid phase.

At the surface of an aqueous electrolyte solution the local electric field responsible for the surface potential may arise from a preferred orientation of the water dipoles in the surface zone, or from an ionic double layer due to the differential desorption or adsorption of cations and anions, or from both together. The equilibrium concentration of charged particles in the gas phase is effectively zero, and for this reason there is no electrical double layer *across* the interface as there can be for example at a mercury-aqueous solution interface.

3.2 Methods of Measurement

There is no method of measuring the absolute value of a surface potential (χ) or of any interface potential. Circumstantial evidence from which we attempt to estimate χ for the liquid–vapour interface of pure water is discussed in Section 4. Changes in χ with change in composition of the liquid phase can be measured, though sometimes only with the aid of rather dubious non-thermodynamic assumptions. Methods of measurement are all based on the same principle, which can be explained with reference to Figure 14. Suppose A to be an electrically conducting aqueous solution, C a dilute gas and B another conducting phase (a gold electrode or an aqueous solution) whose composition will be constant. The inner electrical ("Galvani") potential of each condensed phase will be denoted by ϕ, the outer ("Volta") potential by ψ and $\phi = \psi + \chi$ (see Ref. 56). The inner potential of phase B, ϕ^B, is held constant. Because its composition is constant and if there is no surface contamination, χ^B = constant, therefore ψ^B = constant. Now it is possible to establish experimentally when $\psi^A = \psi^B$. One method of doing this is to ionise the gas C by means of ionising radiation and to detect any current flowing between A and B by the electrometer in the external circuit†. Two other methods are based on the fact that if $\psi^A \neq \psi^B$ there must be a net surface charge on both A and B (+*ve* on one, −*ve* on the other). If B is a metal plate and its distance from A is varied rapidly—vibrating plate method[58]—the

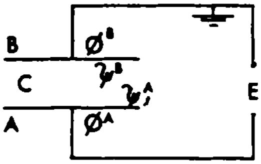

FIGURE 14 Basic circuit used in measurements of surface potential.

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† For a detailed critical assessment of this method see K. W. Bewig *Rev. Sci. Inst.*, 35, 1160 (1954).

pair act as a condenser of varying capacity. If ψ^A is held constant but $\psi^A \neq \psi^B$, an alternating current must flow in the external circuit. Therefore the condition of zero current is the condition for $\psi^A = \psi^B$. Alternatively, *B* may be a liquid jet passing close to the surface of *A* and breaking into droplets as it does so, i.e. Kenrick's method.[59–61] If $\psi^A \neq \psi^B$ there must be a surface charge on the liquid jet which is carried away when it breaks into droplets. Thus again the condition for zero current is the condition for $\psi^A = \psi^B$. Experimentally, for each method, the value of the applied E.M.F., *E*, which corresponds to zero current is found. This is the condition for which

$$\psi^A = \psi^B = \text{constant}.$$

It therefore follows that if χ^A varies

$$\Delta\chi^A = \Delta\phi^A - \Delta\psi^A = \Delta\phi^A \tag{42}$$

and if $\Delta\phi^A$ can be related to ΔE, $\Delta\chi^A$ can be measured.

Two methods of making electrical connection to the electrolyte solution *A* may be used: (1) by means of an electrode reversible to a cation or anion in the solution; (2) by means of an external reference electrode with liquid junction to solution *A*. For example

$$
\begin{array}{lll|cc|lll}
 & & & A & & \text{Na(Hg)} & \phi^{el} & 1(a)\\
(1) & C & \psi^A & & \phi^A & & & \\
 & & & \text{NaBr,(H}_2\text{O)} & & \text{AgBr Ag} & \phi^{el} & 1(b)
\end{array}
$$

$$
\begin{array}{lll|cc|lll}
 & & & A & & \text{KCl(H}_2\text{O)} & & \\
(2) & C & \psi^A & & \phi^A & & \text{HgCl/Hg} & \phi^{el}\\
 & & & \text{NaNO}_3\text{(H}_2\text{O)} & & \text{satd.} & & \\
 & & & & & \multicolumn{1}{l}{\Delta\phi^j} & &
\end{array}
$$

If, to solution *A* a very small amount of a surface active substance is added, χ^A may change with only negligible change in the bulk composition of *A*. In this case $\phi^A - \phi^{el}$ is constant for either (1) or (2), and $\Delta E = \Delta\phi^A = \Delta\chi^A$. If on the other hand we wish to measure the change in χ^A with change of concentration of NaBr in (1), then

$$\Delta\phi^A = \Delta(\phi^A - \phi^{el}) + \Delta E = \frac{-kT}{e_0}\Delta \ln a_+ + \Delta E \qquad 1(a)$$

or

$$= \frac{+kT}{e_0}\Delta \ln a_- + \Delta E \qquad (1b)$$

The single ion activities in these expressions can only be regarded as known at low concentrations for which the "primitive model" of electrolyte solutions is reasonably valid. For 1-1 electrolytes there is probably little error in assuming that $a_+ = a_- = a_\pm$ at concentrations up to 0.1 M. Above this concentration, serious uncertainty about single ion activities in system (1), or about the liquid junction potential $\Delta\phi^j$ in system (2) cannot be avoided. The same problem afflicts the interpretation of glass electrode E.M.F. measurements and has been discussed in connection with pH determination by Bates.[62] The introduction of other cation-reversible electrodes has stimulated further thought on the problem of single-ion activities and liquid junction potentials.[63,64] Two possible assumptions about single-ion activities are usually considered. These are (a) the MacInnes convention[65] and (b) the assumption that in any solution of a single symmetrical electrolyte $\gamma_+ = \gamma_- = \gamma_\pm$ (γ being actively coefficient). The latter is a special case of a more general principle proposed by Guggenheim.[66] The MacInnes convention consists in assuming that $\gamma_{K^+} = \gamma_{Cl^-} = \gamma_+$ in a pure KCl solution of any concentration and that γ_{Cl^-} in any solution of 1-1 electrolytes has the same value as it has in a pure KCl solution of the same ionic strength. In the work mentioned[63,64] it was concluded that the interpretation of the E.M.F.s of cells employing cation-reversible electrodes, with and without KCl (or other) "salt-bridges" is most self-consistent when the MacInnes convention is used to define single ion activities and the Henderson equation to calculate liquid junction potentials. In this work the MacInnes convention was extended, with reasonable logic, to the more general assumption: γ_- of any given anion, or γ_+ of any given cation, has the same value in any solution of 1-1 electrolytes of the same ionic strength. However, this leads to a serious inconsistency since it follows that, for solutions of each of four salts, BX, BY, CX, CY, of equal concentrations, the γ_+'s should be related by

$$\frac{\gamma_\pm(\mathrm{BX}).\gamma_\pm(\mathrm{CY})}{\gamma_\pm(\mathrm{CX}).\gamma_\pm(\mathrm{BY})} = 1 \tag{43}$$

While (43) must be true for any one solution containing all four ions, it is not true for separate solutions of each salt. For example, for 1 M solutions of each salt

$$\frac{\gamma_\pm(\mathrm{KOH}).\gamma_\pm(\mathrm{LiNO_3})}{\gamma_\pm(\mathrm{LiOH}).\gamma_\pm(\mathrm{KNO_3})} = 2.29$$

This fact also shows that a tabulation of single ion activities as a function of ionic strength alone[67] is almost meaningless.

Therefore, if surface potentials are measured by system 1, above, it is probably best to follow the convention that $a_+ = a_- = a_\pm$ for a 1-1 electrolyte at all concentrations as has been done by some workers.[68,69] Alternatively system (2) may be used[60,70] with saturated KCl or similar "salt bridge" and the liquid junction potential is either neglected or where necessary calculated by the Henderson equation. Although these uncertainties cannot be eliminated it is probable that when large differences of solvation or mobility of cations and anions in solution A increase the uncertainty in single ion activities or liquid junction potential, these same differences lead to larger absolute values of $\Delta\chi^A$ in which the probable errors are less important.

In the ionised gas electrode- and the vibrating plate-methods of measuring $\Delta\chi$ the liquid surface under study is normally stationary, while in Kenrick's method it is flowing. For the study of surface potential changes caused by "surfactants" or "insoluble" monolayers only the first two methods allow time for an equilibrium surface to be formed. On the other hand, for the study of surface potential changes due to simple inorganic salts in aqueous solution the continuously renewed surface used in Kenrick's method has the advantage of minimising errors due to traces of surface active materials accidentally present in the solution. Doubts have been expressed about the validity of Kenrick's method.[71] With a proper experimental set-up the only likely source of error is a streaming potential gradient in the capillary forming the liquid jet. This remains present if the out liquid level is raised till it immerses the tip of the jet, and can therefore be detected. It is negligible if the solution in the jet has a concentration greater than 0.05 M.[72] Jarvis and Scheiman[70] compared their results obtained by the ionised gas electrode method, with those obtained by Kenrick's method and concluded that "the two experimental methods are measuring the same surface phenomenon." There is, in fact, no reason to doubt this provided that in Kenrick's method both solutions reach an equilibrium value of $\Delta\chi$ sufficiently rapidly.

The question of the time for formation of an equilibrium surface structure should be mentioned here. The rate of flow of solution down the inside surface of the outer cylinder in Kenrick's method is relatively slow, but that of the jet is rapid. The time between the emergence of the liquid from the capillary and its breaking into droplets is a few milliseconds.[61] Using 0.05 M solutions of NaOH, Na_2SO_4 and KCl, in both the jet and the outer cylinder, asymmetry potentials of less than 1 mV were found.[72] This shows that if there is an appreciable surface potential due to preferred orientation of water molecules in the surface zone, then it has reached its equilibrium value within 1 millisecond. The contribution to the surface potential made by the 0.05 M concentrations of the electrolytes mentioned is very small and if there were a time lag in its development it would probably not have been detected. However, the time of formation of the ionic double layer in solutions of small simple ions can be assumed to be comparable with the relaxation time of the ordinary ionic atmosphere in the bulk solution. In a 0.05 M solution of a 1–1 salt in water this is less than 10^{-8} sec and decreases with increasing concentration. On the other hand the time required to develop an equilibrium surface structure when, for example, long paraffin chain surfactant ions are involved would almost certainly be longer than the lifetime of the surface of the liquid jet in Kenrick's method. As for the time of formation of an equilibrium water structure at the liquid surface, surface potential measurements agree with the balance of evidence from dynamic surface tension measurements (Section 1–4) in indicating that it is less than a millisecond. If it is comparable with the dielectric relaxation time, then of course it is many powers of ten less than a millisecond.

3.3 Results of Surface Potential Measurement

In general for aqueous electrolyte solutions, the change of χ with change of concentration is measured and extrapolated to infinite dilutions. The results are then expressed as $\Delta\chi = \chi\,(\text{solution}) - \chi\,(\text{pure water})$. The dependence of $\Delta\chi$ on concentration for some common salts and acids is shown in Figure 15.

In the interpretation of surface potentials we can assume that $\Delta\chi$ may contain contributions from three sources. These are (a) an ionic double layer resulting from a difference between the accessibility of the surface zone to anions and to cations; (b) a preferred orientation near the surface, of solute ions having permanent dipoles, or of ion-pairs or molecules derived from the solute; (c) a change in the average orientation of water molecules in the surface zone from that in pure water. It is probable (see Section 4.2) that the surface potential of pure water is small and that the molecules in the surface zone have only a weakly preferred orientation along the normal to the surface. It is therefore likely that under the influence of ions or solute dipoles they will respond mainly passively, i.e. as a dielectric tending to diminish the

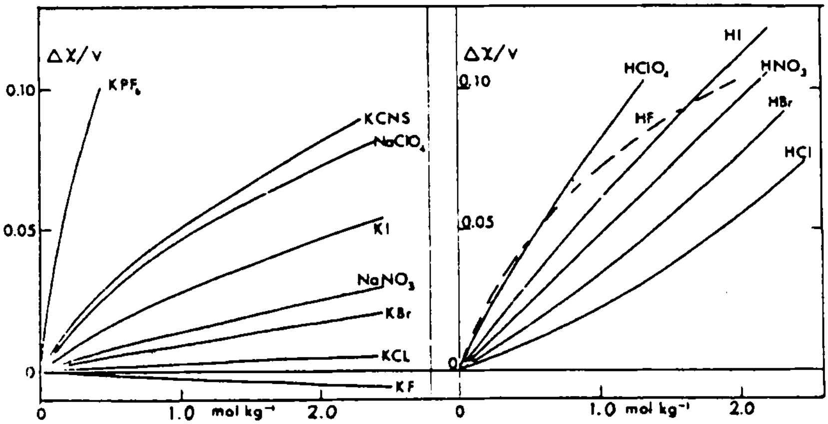

FIGURE 15 Surface potential increments, $\Delta\chi$, of some 1-1 salts and acids in water, plotted against molality.

potential drop due to factors (a) or (b) above, rather than making a characteristic (i.e. unsymmetric) contribution of their own. A suggestion[73] that (c) was the major contributor to $\Delta\chi$ was shown by Frumkin[74] to be almost certainly wrong.

On this basis the positive $\Delta\chi$ exhibited by most alkali metal salts appearing in Figure 15 implies an ionic double layer near the surface with its positive side directed into the bulk liquid. Hence, of the anions and cations shown, in all cases, with the exception of *KF*, the anions approach the surface more easily. (KOH gives a similar negative $\Delta\chi$). For the alkali metal salts the magnitude of $\Delta\chi$ depends almost entirely on the anion and very little on the cation. For example, at a concentration of 3 M the $\Delta\chi$ values for LiCl, NaCl, KCl and CsCl are +13, +9, +6 and +6 mV respectively. Substitution of alkaline earth cations for alkali cations also has little effect on $\Delta\chi$.[70] However, replacement of the alkali cation by hydrogen ion causes a considerable positive shift of $\Delta\chi$. Thus for 1 M solutions the shifts are as follows:[60,69]

TABLE III

$\Delta(\Delta\chi) = \Delta\chi(\mathrm{HX}) - \Delta\chi(\mathrm{MX})$ for 1 M solutions

$X^- =$	F^-	Cl^-	Br^-	NO_3^-	I^-	ClO_4^-	
$\Delta(\Delta\chi) =$	84	20	25	34	33	34	mV

The order in which the anions are listed is that of increasing $\Delta\chi(\mathrm{MX})$ from left to right. The value of $\Delta(\Delta\chi)$ for F^- is obviously abnormal. This is almost certainly due to the weakness of HF as an acid, and to molecular HF or $(HF)_2$ being surface active. Some HF^- may also be present. The implication of the large positive $\Delta\chi$ of HF solutions is that these species adsorb with the proton end of the molecule (or ion) directed into the liquid. Surface tension data for HF solutions do not appear to be available but would almost certainly indicate adsorption of the acid (compare HCl, Section 2.5).

There remains, however, a paradox with respect to the surface potentials of the other acids. There is evidence from surface tension changes (Section 2.5) that in HCl solutions at concentrations above 0.1 M undissociated acid molecules are present in the surface zone, but no evidence that this is the case for HNO_3, $HClO_4$ and HPF_6, which are stronger acids. Hence it would seem that it must be the ionic double layer in the surface of these strong acid soltuions which gives rise to a larger $\Delta\chi$ than does that of the corresponding alkali metal salt solutions. This requires that the hydrogen ion is repelled from the surface more strongly than are the alkali cations. However, surface tension measurements (Section 2.5) show conclusively that these acids are less, and not more, strongly desorbed from the surface than are the alkali metal salts. Indeed, the differences are such as to suggest that H_3O^+ easily penetrates into the uppermost molecular layer of the transition zone, and may even be attracted into it. This being so, the large positive $\Delta\chi$ is mysterious and the only hypothesis to explain it seems to be that H_3O^+ ions in the surface are preferentially oriented with their protons directed into the liquid phase. The dipole moment of H_3O^+ is probably similar to that of a water molecule,[75] but it may be that the orientation of neighbouring water molecules is influenced in such a way as to enhance the effect of the H_3O^+ dipole itself. All this is in line with what has been suggested for the orientation of HF in the surface, but to counter this it must be admitted that ammonia dissolved in water is surface active but causes a considerable negative $\Delta\chi$. This is the reverse of what would be expected if NH_3 in the surface had a preferred orientation with the protons directed into the liquid.

3.4 Anion Adsorption

The small values of $\Delta\chi$ for aqueous KF, KOH and KCl (Figure 15) show that in these solutions the distance of closest approach to the surface is about the same for anions as it is for cations. The surface excess of water in the solutions corresponds to an ion-free layer comprising about 1 monolayer of water molecules (Table II). From this we deduce that K^+, OH^-, F^-, Cl^- retain at least the first layer of their hydration shell when they approach the surface. The positive $\Delta\chi$ and smaller y values (Table II) of other salts such as KI, $NaClO_4$, KCNS show that other anions are less strongly desorbed. The most likely interpretation is that at the surface of solutions of these salts a proportion of the anions penetrate into the uppermost molecular layers of the transition zone (which would otherwise be the ion-free layer) losing all their hydration shell on the gas–phase side. These ions we shall regard as adsorbed. In the layers below there is an excess of cations, equivalent to the adsorbed anions, which constitute a diffuse layer charge. The distinction between "adsorbed" and "diffuse layer" ions cannot be made as precisely as it can for ions at an electrolyte solution-mercury interface. Nevertheless this simple model helps us to understand the electrical behaviour of the solution–gas interface and to compare it with the interface with mercury.

If we plot $\Delta\chi$ for electrolytes whose anions are "adsorbed" against $(RT/F)\ln a_\pm$ we get the curves shown in Figure 16. These graphs are the analogues of the Esin–Markov curves for the electrolyte solution–mercury interface and they likewise show the Esin–Markov effect.[76,77] This "effect" is in essence the rather surprising fact that the negative shift of the potential of zero charge of mercury in contact with a solution of, say, KI, with increasing concentration of the salt, is greater than that of an electrode reversible to the anion. It is easy to see that this is unexpected if the adsorbed anions are treated as "smeared-out" layer of charge. Let ϕ' be the electrical potential

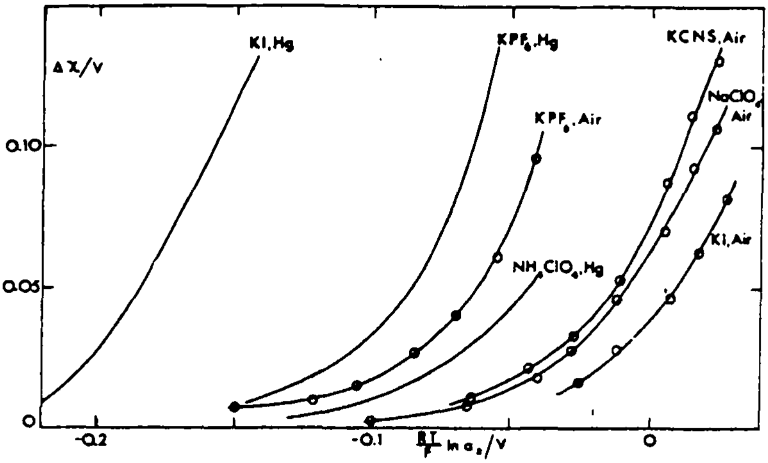

FIGURE 16 $\Delta\chi$ as a function of $(RT/F)\ln a_\pm$ for several 1-1 salts. For comparison, the shift of the e.c.m. potential of mercury, $-\Delta\phi^{\mathrm{Hg-s}}_{\mathrm{ecm}}$, in aqueous KI, KPF$_6$ and NH$_4$ClO$_4$ solutions is plotted against the same function of $a_\pm$; data from D. C. Grahame, *J. Amer. Chem. Soc.*, **80**, 4201 (1958) and E. Dutkiewicz and R. Parsons, *J. Electroanal. Chem.*, **11**, 100 (1966); G. J. Hills and R. M. Reeves, ibid. 31, 269 (1971); R. Payne, *J. Phys. Chem.*, 70, 204 (1966).

in the plane of the adsorbed anions and ϕ^s that in the bulk solution. If we equate the electrochemical potential of the adsorbed anions to that of the anions in the bulk solution then (for monovalent anions)

$$\mu'_- - \phi' e_0 = \mu^s_- - \phi^s e_0$$

hence

$$e_0 \frac{\mathrm{d}(\phi^s - \phi')}{\mathrm{d}\ln a^s_-} = \frac{\mathrm{d}(\mu^s_- - \mu'_-)}{\mathrm{d}\ln a^s_-} = kT\left(1 - \frac{\mathrm{d}\ln a'_-}{\mathrm{d}\ln a^s_-}\right) \tag{45}$$

where a^s_- is the activity of the anions in the bulk solution and a'_- that of the adsorbed anions. If the adsorbed anions are treated as a smeared out layer of charge there is no field above this layer since there is no charge above it. Hence

$$\mathrm{d}(\Delta\chi) = \mathrm{d}(\phi^s - \phi') \tag{46}$$

It follows from (45) and (46) that

$$\mathrm{d}\Delta\chi < \frac{kT}{e_0}\mathrm{d}\ln a^s_- \tag{47}$$

unless d ln a'/d ln a^s_- is negative—i.e. the activity or concentration of adsorbed anions decreases as the bulk concentration increases—which is unlikely†. For an electrode reversible to anions in the solution

$$d(\phi^s - \phi^{el}) = \frac{kT}{e_0} d \ln a^s_-$$

equivalent to the situation when a'_- is constant. Inspection of Figure 16 shows that at high concentrations the slope of $\Delta\chi$ vs. $(kT/e_0)\ln a_\pm$ is greater than unity for several salts. Curves of $(\phi^s - \phi^{\mathrm{Hg}})_{q^m=0} = -\Delta\phi^{\mathrm{Hg-S}}_{\mathrm{ecm}}$ for KI and KPF_6 solutions are included for comparison.

The thermodynamic implications of the Esin–Markov effect have been fully discussed by Parsons.[77] He has shown that for the electrolyte solution–mercury interface it is closely related to the dependence of the surface concentration of adsorbed anions on the charge density on the mercury, at constant solution composition. At an electrolyte solution–air interface the net charge in the solution phase is compelled to be zero (because that in the air phase is zero) so that this approach is not applicable. With regard to the electrostatic model of the interface, the Esin–Markov effect shows that it is inadmissible to regard the adsorbed ions as a smeared out layer of charge. This was recognised by Esin and Shikov[78] and a more detailed discrete charge model was developed by Ershler.[79] Since then there has been a large amount of theoretical work on the "discreteness of charge effect." The subject has been very fully reviewed by Barlow and Macdonald[80] and this work should be consulted for details. It would not be appropriate to attempt to apply to the electrolyte solution–air interface an elaborate mathematical treatment such as those which have been used in studies of the solution–mercury interface. To the present writer these theories look rather top-heavy. The physical model, in which macroscopic concepts such as dielectric constant have to be used in a molecular scale problem, hardly seems to justify so elaborate a mathematical superstructure. Be that as it may, I shall for the present purpose do no more than assume some quantitative consequences of the discrete charge model and interpret the experimental results for the solution–air interface in terms of them.

In the first place the discrete charge model makes it clear that the difference between the average potential ϕ' in the plane of the centres of the adsorbed ions, and that in the bulk solution is considerably less than the total potential difference attributable to the ionic double layer (see Figure 17). In addition the micro-potential at the centre of an adsorbed ion is not the same as the average potential ϕ'. The overall result is that the increase of $\Delta\chi$ with increasing electrolyte concentration (Figure 16) can be very much larger than the

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† For a more detailed treatment of this argument see Ref. 56.

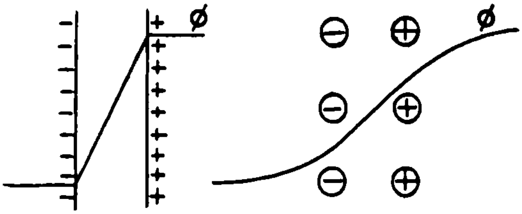

FIGURE 17 Diagram of the profile of the electrical potential change across two parallel planes of "smeared-out" charge, and across two parallel planes containing discrete charges.

smeared-out charge model permits (Eq. (47)), thus explaining the Esin–Markov effect.

Further understanding of anion adsorption requires that we should know the surface concentration of adsorbed ions. At a solution–mercury interface the net charge density on the mercury is available as a variable and use of this, together with diffuse layer theory, enables the concentration of specifically adsorbed ions to be determined. At a solution–air interface since net charge density is not available as a variable the surface concentration of adsorbed ions must be estimated in a more approximate way.

In a solution of a 1–1 electrolyte, MX, let there be n'_- adsorbed anions per cm^2 of surface. These ions as already defined occupy positions in the uppermost molecular layer of the liquid-gas transition zone, which would, in a solution of a non-adsorbed electrolyte be part of the ion-free layer. The complementary positive charge consists of an excess of $\tau_+ n'_-$ cations and a deficit of $(1 - \tau_+)n'_-$ anions, per cm^2, in the diffuse layer below. τ_+ is the transference number of cations in the diffuse layer.[81] Compared with the amount of salt which would be present at the surface of a solution of a non-adsorbed electrolyte with the same thickness of ion free layer, there is therefore a net excess of $\tau_+ n'_-$ molecules of MX per cm^2. Taking into account the water displaced by the excess ions, $\tau_+ n'_-$ is related to the thermodynamic surface excess of solute relative to solvent by

$$\left(1 + \frac{m v_2}{55.5 v_1}\right)\tau_+ n'_- = \Gamma_{2(1)} - \Gamma^{na}_{2(1)} \qquad (48)$$

Here m is the bulk molal concentration of MX, 55.5 is the number of moles in 1 Kgm of water and v_1 and v_2 are the apparent molal volumes of water and MX respectively. $\Gamma_{2(1)}$ is the thermodynamic surface excess of MX relative to water, and $\Gamma^{na}_{2(1)}$ is the same for a non-adsorbed electrolyte at the same concentration. From Eq. (34)

$$\Gamma_{2(1)} = \frac{-m}{55.5}\Gamma_{1(2)} = \frac{+m}{55.5}\frac{d\gamma}{d\mu_1}$$

Since also, (Eq. 38)

$$\mathrm{d}\mu_1 = kT\mathrm{d}\ln a_1 = -\frac{kT}{55.5}\mathrm{d}(\nu m\phi)$$

hence

$$\Gamma_{2(1)} = -mkT\frac{\mathrm{d}\gamma}{\mathrm{d}(\nu m\phi)}$$

Using this equation, Eq. (48) becomes

$$\tau_+ n'_- = mkT\left(\frac{\mathrm{d}\gamma^{na}}{\mathrm{d}(\nu m\phi)} - \frac{\mathrm{d}\gamma}{\mathrm{d}(\nu m\phi)}\right)\left(1 + \frac{mv_2}{55.5v_1}\right) \tag{49}$$

Thus $\tau_+ n'_-$ can be obtained from the slopes of curves such as those plotted in Figure 10. The curve for γ^{na} was plotted from data for KCl and NaCl (Jones and Ray) and for KF (Heydweiller[34]) which fall closely on a single curve. τ_+ was calculated from diffuse layer theory enabling n'_- to be determined.

The results show that the adsorption of anions at the interface between an electrolyte solution and air has similarities to that at an interface with mercury. In Figure 18 $\Delta\chi$ is plotted against surface concentration of adsorbed anions, expressed as charge density q'_-. At an interface with mercury the quantity corresponding to $\Delta\chi$, $-\Delta\phi^{\mathrm{Hg-s}}_{\mathrm{ecm}}$, is proportional to q'_- and the slopes for KI and for KPF_6 as indicated in Figure 18 are similar to those for the solution–

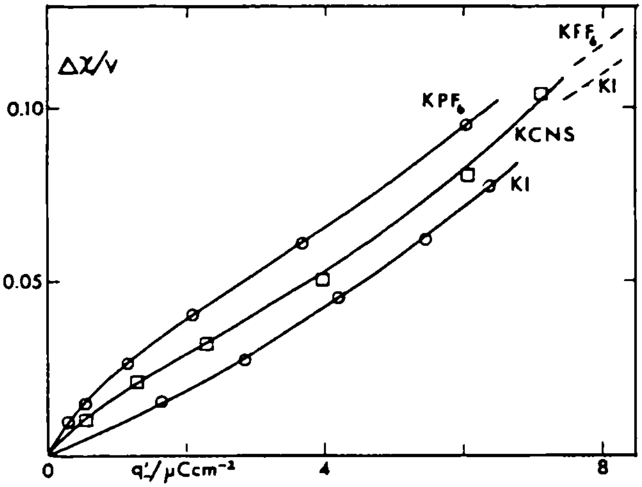

FIGURE 18 $\Delta\chi$ plotted against the "adsorbed" charge density calculated by equation (49) from surface tension data. The two short broken lines denote the slope of $-\Delta\phi^{\mathrm{Hg-S}}_{\mathrm{ecm}}$ with adsorbed charge, in solutions of KI, data from D. C. Grahame, *J. Amer. Chem. Soc.*, **80**, 4201 (1958), and KPF_6, data from G. J. Hills and R. M. Reeves, *J. Electroanal. Chem.*, 31, 269 (1971).

air interface. This is slightly surprising in that one would expect the mercury to suppress the potential gradient on its side of the interface; it may be that a greater mobility of the water molecules at the solution–air interface compensates for this.

There has been much discussion of "isotherms" of adsorption of anions at the electrolyte solution–mercury interface.[82] At low surface concentrations of adsorbed anions it can be assumed that their activity a'_- is proportional to their concentration n'_- (or to q'_-). This is the "Henry's law" domain; at higher concentrations mutual interactions between adsorbed anions, or their electrical images, are expected to modify this simple relationship. Let us assume as before that at equilibrium the electrochemical potential of the adsorbed anions equals that of the anions in the bulk solution

$$\bar{\mu}'_- = \bar{\mu}^s_- \tag{50}$$

If ϕ'' is the micro potential at the site of an adsorbed anion relative to that in the bulk solution, then while Henry's law is obeyed,

$$kT \ln n'_- - e_0\phi'' = kT \ln a^s_- - e_0\phi^s + \text{const.}$$

or

$$\frac{kT}{e_0} \ln \frac{n'_-}{a_\pm} = (\phi'' - \phi^s) + \text{const.} \tag{51}$$

where we have replaced a^s_- by $a_\pm$. It has been argued[83] that, because at constant net surface charge the adsorption of an anion must be accompanied by an equal gain of positive charge by the diffuse layer, we are really concerned with adsorption of salt, MX. If this is so, the argument continues, Eq. (51) should be replaced by

$$\frac{kT}{e_0} \ln \frac{n'_-}{a^2_\pm} = (\phi'' - \phi^s) + \text{const.} \tag{51a}$$

Alternatively it has been proposed[84] that $a^{(2\tau_+)}_\pm$ should be used since the net adsorption of salt is τ_+ molecules of MX per adsorbed anion. A detailed discussion would be out of place here, but in the present writer's opinion the addition of charge to the diffuse layer which must accompany the adsorption of an anion may have the effect of raising $a_\pm$ in Eq. (51) to a power slightly greater than one, but certainly not to $a^2_\pm$.

In Figure 19 experimental values of n'_- calculated by means of Eq. (49) have been used to plot $(kT/e_0)\ln n'_-/m$, $(kT/e_0)\ln n'_-/a_\pm$ and $(kT/e_0)\ln n'_-/a^2_\pm$ against $\Delta\chi$. The graphs of the first quantity have negative slopes between a quarter and a half, which would imply $\Delta(\phi^s - \phi'')$ between a quarter and a half of $\Delta\chi$, which is reasonable. For the second quantity the slopes are too small. For the third quantity the negative slope is greater than 1 at low concentrations,

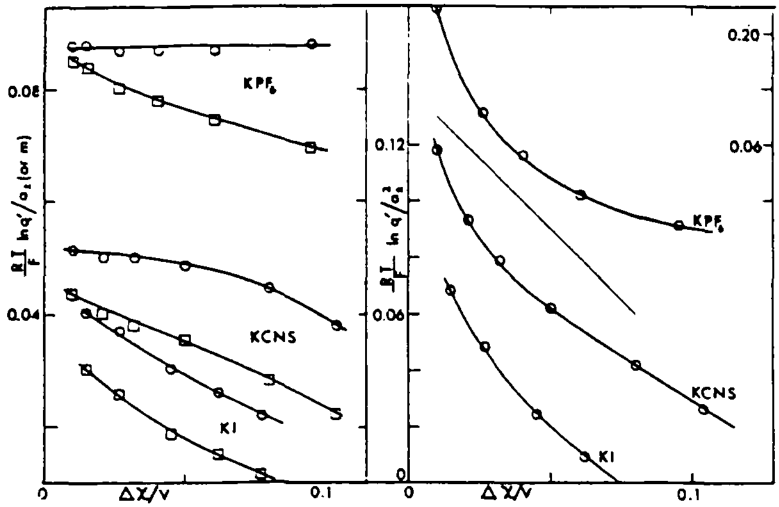

FIGURE 19 Left: Experimental points: ○$(RT/F)\ln q^1_-/a_\pm$, □$(RT/F)\ln q^1_-/m$, plotted against $\Delta\chi$.
Right: $(RT/F)\ln q^1_-/a^2_\pm$ plotted against $\Delta\chi$; the right hand scale of ordinates refers to KPF$_6$; the straight line has a slope of -1.

which means that $\Delta(\phi^s - \phi'') > \Delta\chi$, which is impossible for any simple model. The use of n'_-/m in the first quantity might be justified by saying that the activity coefficient of an adsorbed anion is similar to that of one in the bulk solution, but a better representation can probably be obtained by a consideration of the total adsorption process.

While the general shape of the adsorption isotherm for anions at the solution-air interface is similar to that for the solution–mercury interface, the strength of the adsorptive forces differs markedly for some ions, though not for others. For example, the curves of $\Delta\chi$ and of $-\Delta\phi^{Hg-S}_{ecm}$ for PF_6^- (in Figure 16) rise at similar concentrations of PF_6^- in solution. Therefore the standard free energies of adsorption of this anion at the two interfaces are similar. Inspection of Figure 16 shows that the same is true of ClO_4^-. It seems that the adsorption of these ions must be due to some unfavourable feature of hydration of the ions in the bulk solution which makes an interface a preferred environment. This is the phenomenon termed "out-squeezing" by D. C. Grahame. There is no indication of any specific interaction between these ions and mercury†.

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† The preference for an interface exhibited by these ions may be similar to the tendency commented on by Gurney,[86] of structure breaking ions to associate with each other. For example, there is marked ion association in aqueous KPF$_6$ solution[85] ($\gamma_\pm = 0.45$ in 0.5 M solution) as there is between K$^+$ and NO$_3^-$, and even between Cs$^+$ and I$^-$ ($\gamma_\pm$ of CsI $= 0.43$ at 3.0 M, compare $\gamma_\pm$ of LiI $= 1.42$ at 3.0 M).

In contrast to the above the strength of adsorption of iodide ion is very different at the two interfaces. There is a separation between the $\Delta\chi$ and $-\Delta\phi_{ecm}^{Hg-S}$ curves in Figure 16 equivalent to a solution concentration ratio greater than 10^3. Probably at the solution–air interface the adsorptive forces are similar in kind to, though weaker than, those which operate on PF_6^- and ClO_4^-. At the mercury interface there are strong specific adsorptive forces which are generally assumed to be due to incipient formation of an Hg–I covalent bond.

3.5 Adsorption of Cations

The quaternary ammonium cations, NR_4^+ where R is an alkyl radical become increasingly surface active as the number of carbon atoms in R increases. The strongly surfactant properties of long chain quaternary ammonium ions are well known. The dependence of $\Delta\chi$ on concentration for solutions of the chlorides of NMe_4^+ and NEt_4^+ is shown in Figure 12. The existence of an ionic double layer, negative inwards, is clearly indicated by the negative values of $\Delta\chi$. The surface tension curves for the tetra-alkyl ammonium salts also shown in Figure 12 are based on not very precise data. However, it is interesting to note that while the net adsorption of NEt_4Cl is less than that of KPF_6, as indicated by the $\Delta\gamma$ curves, the magnitude of $\Delta\chi$ is greater for NEt_4Cl. The same is true of the pair NMe_4Cl and KCNS. It is possible that this lack of symmetry, i.e. that adsorption of a cation gives a larger shift of χ than does the equivalent amount of adsorption of an anion, is due to the existence of a preferred orientation of water molecules in the surface of pure water. If so, then the preferred orientation required is with the positive ends of the water dipoles inwards, so that for pure water χ^{H_2O} would be positive. However, the evidence does not justify any stronger statement than that it is compatible with χ^{H_2O} being positive. The probable value of χ^{H_2O} is discussed in detail in Section 4.

CONCLUSIONS

All ions in dilute aqueous solution are repelled from the solution–gas interface by an image force repulsion which can be calculated by the methods of Onsager and Samaras, or Buff and Stillinger. Two other kinds of forces are important. One of these is the strong interaction of all monatomic cations, and some anions, with the first, or first two, layers of water molecules in the hydration shell. These firmly held water molecules are not lost when the ion approached the surface, and the effect on the surface tension can be interpreted as due to an ion-free layer of one (or two) monolayers of water molecules at the surface. In solutions of these ions at concentrations over 0.1 M the contribution of the ion-free layer to the surface deficit of ions becomes much larger than the calculated contribution due to image force repulsion. The second type of force is an adsorptive force which becomes important for large anions or cations. This can result in net adsorption, in spite of image force repulsion, even at low concentrations. These forces can operate when the gradient of electrical field strength at the surface of the ion is small so that the adjacent water dipoles are not firmly held. They must be related to the influence of the ion on the structure of water around it, and may be labelled, without a pretence at understanding, with Grahame's word, "out-squeezing" forces.

4 THE SURFACE POTENTIAL OF PURE WATER

4.1 Estimation from the 'Real' and 'Chemical' Free Energies of Hydration of Ions

The absolute value of the surface potential of water χ^{H_2O} (as of any other condensed phase) cannot be measured. It is not inconceivable that a method may be found of assessing the average orientation of the water molecules near the surface, relative to the plane of the surface, but none is known at present. It is therefore only possible to estimate χ^{H_2O} from indirect evidence†. Most of such estimates have been based on the relationship, first pointed out by Frumkin[87] and by Lange and Mischenko,[88] between the "real" free energy of hydration of an ion, $\alpha_i^{H_2O}$, and the "chemical" free energy of hydration $\Delta\mu_i^{H_2O}$. The former is the free energy of transfer of an ion from a dilute gas phase through the surface of water into the bulk liquid. It is made up of the work of transmission through the surface, $z_i e_0 \chi^{H_2O}$, where z_i is the electrovalence of the ion, and the "chemical" free energy of hydration, $\Delta\mu_i^{H_2O}$,

$$\alpha_i^{H_2O} = \Delta\mu_i^{H_2O} + z_i e_0 \chi^{H_2O} \tag{52}$$

The "real" free energy of hydration can be obtained from measurements of the E.M.F. of the cell

$$\text{Hg}\left|\begin{matrix}\text{HgCl KCl}_{\text{aq}}\\ a_{\pm}\end{matrix}\right|\begin{matrix}\text{inert}\\ \text{gas}\end{matrix}\left|\text{Hg}\right.$$

under the condition that $\psi^{\text{solution}} = \psi^{\text{Hg}}$ using either an ionising electrode in the

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† Some attempts at direct measurement were made, usually based on the misconception that it was possible to produce an aqueous surface with zero surface potential, e.g. a wet filter paper as used by Chalmers and Pasguil (*Phil. Mag.*, 23, 88 (1937)).

gas, or the Kenrick method with a mercury jet.[61,89] Using the electron work function of mercury and assuming that $a_{Cl^-} = a_{\pm}$ in the electrolyte solution, $\alpha^{H_2O}_{K^+}$ can be found. The standard free energy for transfer of K$^+$ from the ideal gas phase at 1 atm pressure to the ideal 1 M solution at 298 K was found[61] to be

$$\begin{aligned}\alpha^{\circ H_2O}_{K^+} &= -80.6 \pm 0.5 \text{ k cal mol}^{-1}\\ &= -5.60 \pm 0.04 \times 10^{-14} \text{ erg. molecule}^{-1}\end{aligned}$$

The error may be slightly greater than that stated but is unlikely to exceed $\pm$ 1 k cal mol^{-1} (for ease of comparison with the original work in all of which the data is recorded in k cal mol^{-1}, I shall use these units throughout this Section).

Free energies of hydration of ions from the gas phase can also be obtained from thermodynamic data for pairs or groups of ions of zero net charge (such as $K^+ + Cl^-$ or $Ca^{2+} + 2Cl^-$). Since for such a group $\Sigma z_i = 0$, it follows from (52) that

$$\text{Thermodynamic free energy of hydration} = \Sigma\Delta\mu_i^{H_2O} = \Sigma\alpha_i^{H_2O}$$

Thus when $\alpha_i^{\circ H_2O}$ is known for one ion it can be found for all ions for which the thermodynamic data is available. The value for the proton derived from that for K$^+$ is

$$\alpha^{\circ H_2O}_{H^+} = -260.5 \pm 0.5 \text{ k cal mol}^{-1}$$

It is still impossible to determine χ^{H_2O} by Eq. (52) until at least one single-ion "chemical" free energy of hydration is also known. This requires the partition of the free energy of hydration of a pair of ions, say $M^+ + X^-$, into the contributions $\Delta\mu^{H_2O}_{M^+}$ and $\Delta\mu^{H_2O}_{X^-}$. Many efforts have been made to find a sound basis for such a partition. The thermodynamic data and the methods of subdivision have been discussed by Halliwell and Nyburg[90] and reviewed fully by Rosseinsky.[91] Unfortunately, the latter does not distinguish between $\alpha_i^{H_2O}$ and $\Delta\mu_i^{H_2O}$, remarking that "for simplicity, ψ^{H_2O} ($\equiv \chi^{H_2O}$) is here summarily taken as zero, from an estimate[92] of 0.1 $\pm$ 0.1 V." The field has also been critically examined by Conway[93] with particular reference to the energy of hydration of the proton.

It is, I think, fair to say that up to the present the disagreement between different assessments of single-ion chemical hydration energies is such that one cannot, with any confidence, derive from them even the sign of χ^{H_2O}, still less its magnitude. Some representative values of χ^{H_2O} obtained by different workers, or deduced from their values of single-ion hydration energies, are listed in Table IV:

TABLE IV

Source	χ^{H_2O}/V
Bernal and Fowler[94]	
Elay and Evans[95]	+0.5
Verwey[96]	−0.48
Passoth[97]	+0.29
Latimer, Pitzer and Slansky[98]	−0.34
Halliwell and Nyburg[90]	−0.39
Izmailov[100]	−0.17
Noyes[99]	−0.08
Salomon[103]	−1.1
Stokes[106]	+0.20
De Ligny, Alfenaar and van der Veen[107]	−0.30

The division made by Bernal and Fowler[94] and the practically equivalent one by Eley and Evans[95] was based on the assumption that $\Delta\mu^{\circ H_2O}_{K^+} = \Delta\mu^{\circ H_2O}_{F^-}$ since the two ions have almost the same crystallographic radius (Pauling). This leads to $\Delta\mu^{\circ H_2O}_{K^+} = 92.2$ kcal mol^{-1}, which together with the value of $\alpha^{H_2O}_{K^+}$ already given, leads to $\chi^{H_2O} = +0.5$ V. A rather more detailed model of the interaction of cations and anions proposed by Verwey[96] led him to the belief that $\Delta\mu^{\circ H_2O}_{F^-} \sim \frac{3}{2}\Delta\mu^{\circ H_2O}_{K^+}$, and the consequent change in these hydration energies changed χ^{H_2O} by almost 1 volt (the value given in Table IV is that estimated by Verwey himself, using Klein and Lange's[89] values for real energies of hydration). Passoth[97] based his division of hydration energies on a correlation with apparent molal volumes of ions derived from earlier work by Webb.[48] Latimer, Pitzer and Slansky[98] based their sub-division on the well-known Born[104] equation:

$$\Delta\mu_i^{el} = \frac{-(z_i e_0)^2}{2r_i}\left(1 - \frac{1}{\varepsilon}\right) \tag{53}$$

This gives the electrostatic free energy of transfer of a sphere of radius r_i and charge $z_i e_0$ from a vacuum into a uniform structureless dielectric medium of dielectric constant ε, and with zero surface potential. If the crystallographic radius of an ion is used for r_i and the macroscopic dielectric constant of water is used for ε, the calculated hydration energies for pairs of ions are considerably larger in magnitude than the thermodynamic values. One reason for this is that the water becomes dielectrically saturated near the ion. Secondly, gaps between the water molecules and the ion in the very high field region close to the ion behave as regions of unit dielectric constant.[101] Both of these reduce the magnitude of the solvation energy. Latimer *et al*[98] took the view that at least the solvation energy of a series of ions of the same charge should vary linearly with $(r_i + \delta)^{-1}$ where r_i is the crystallographic radius and δ takes into account the spaces between the water molecules and the ions. Thus with a properly chosen value of δ_+ the thermodynamic solvation energies of the alkali metal salts of a given anion (say chloride) should vary linearly with $(r_+ + \delta_+)^{-1}$. Correspondingly with an appropriate choice of δ_- the solvation energies of the halides of a particular alkali cation should vary linearly with $(r_- + \delta_-)^{-1}$. By choosing $r_+ = 0.85$ Å and $r_- = 0.1$ Å, straight and also parallel lines were obtained, and the vertical height difference between these gave the difference of solvation energies of the common cation and the common anion. Since the sum of those is also known, the individual values can be obtained. Approximately similar graphical or extrapolation procedures were used by Halliwell and Nyburg, Izmailov,[100] Blandamer and Symons,[102] Noyes[99] and Salomon.[103] Blandamer and Symons used a new set of ionic radii due to Gourary and Adrian.[105] They found that single-ion solvation energies based on the partition $\Delta\mu^{\circ H_2O}_{Rb^+} = \Delta\mu^{\circ H_2O}_{Cl^-}$ fell on a single line when plotted against $(r_{G.A})^{-2}$. Halliwell and Nyburg[90] used the novel idea of focussing attention on the difference between conventional hydration energies of pairs of anions and cations rather than between ions of the same sign. (A "conventional" hydration energy is one expressed on the arbitrary scale defined by $\Delta\mu^{\circ H_2O}_{H^+} = 0$). Salomon[103] used Gourary and Adrian ionic radii and an extrapolation procedure rather similar to, but less convincing than, that of Halliwell and Nyburg. The value of γ^{H_2O} which it yields is far from the average and must be regarded with suspicion.

The fundamental difficulty in all this work is the fact that, on the basis of very inexact theory, or by largely empirical graphical methods, an attempt is made to divide the large hydration energy for a pair of ions (from 129 k cal for $Cs^+ + I^-$ to 226 k cal for $Li^+ + F^-$) into single-ion hydration energies with an accuracy of a few k cal. An error of 4.6 k cal in the division represents an error of 0.2 volt in χ^{H_2O}. Almost always the ionic radius, because of its role in the Born equation, must figure largely in these methods. A very valid objection to the usual way in which the ionic radius is used has been stated by Stokes.[106] The Born hydration energy (Eq. 53) can be written as

$$\Delta\mu_i^{el} = \frac{z_i e_0^2}{2r_i\varepsilon} - \frac{z_i e_0^2}{2r_i}$$

where the first term is the electrostatic self-energy of the ion in the medium of dielec. const. ε, while the second is that of the ion in vacuo. Since $\varepsilon \gg 1$ the second term is much larger than the first and it is very important to have the correct value of r_i in the gas phase. Stokes suggested that the crystal radius of the ion (whichever crystal radius is used) is not appropriate, since in a crystal the ions are subject to considerable compression which is not present in the gas. He therefore calculated the radii of the alkali metal and halogen ions in the gas phase from the known van der Waals radii of the iso-electronic inert gas atoms. The radii he obtained were from 20% to 40% greater than the Pauling crystal radii, and this correspondingly reduces the calculated Born hydration energy. The effect is the same as is obtained by using an increased ionic radius in the Born equation on the basis of "gaps"[101] between the ion and the water molecules in the solution phase, but the reasoning is different and appears to be more compelling.

It might be argued that the self energy of an ion in the gas phase is not part of the experimental data, and its introduction must involve a fallacy, but this is not true since the relevant part of the experimental data is, for an alkali metal ion, the ionisation potential of the atom in vacuo, and the value of this clearly includes the electrostatic self-energy of the ion produced. The same applies to the electron affinity of a halogen atom. In my view Stokes's calculations are rather more convincing than those of Glueckauf or of Latimer Pitzer and Slansky, in both of which "adjusted" ionic radii were used. However, it was necessary for Stokes, as for others, to represent the interaction of an ion with its near-neighbour water molecules as an interaction with a structureless dielectric of arbitrarily chosen ε. The concordance of the χ^{H_2O} values obtained from Stokes's individually calculated $\Delta\mu^{H_2O}$ values for several ions is quite good, except for F^- and I^-, as can be seen from Table V.

TABLE V

	Na^+	K^+	Rb^+	Cs^+	F^-	C^-	Br^-	I^-	
$-\alpha_i^{oH_2O}$	98.2	80.6	75.5	67.5	103.8	75.8	72.5	61.4	k cal mol^{-1}
$-\Delta\mu_i^{oH_2O}$	103.4	85.5	80.0	72.6	81.1	68.6	67.8	61.1	
$F\chi^{H_2O}$	5.2	4.9	4.5	5.1	(22.7)	7.2	4.7	(0.3)	k cal
χ^{H_2O}(mean) = +0.20 V									

An attempt has been made by De Ligny, Alfenaar and van der Veen[107] to obtain χ^{H_2O} by using the Born equation for a direct calculation of the electrical part of the free energy of hydration of a large ion. The ion was the ferricinium cation Fec^+ whose average radius these authors took to be 3.8 ± 0.2 Å (see Ref. 108). It was assumed that the Born equation, using this ionic radius and the macroscopic dielectric constant of water, would give the difference between the "chemical" free energy of hydration of Fec^+ and that of the ferrocene molecule, which is structurally similar. In addition the measured E° for the ferricinium ion-ferrocene half reaction in aqueous solution, the gas–phase ionisation potential of ferrocene, and the known value of $\alpha_{H^+}^{H_2O}$, are sufficient to give the difference between the real free energy of hydration of Fec$^+$ and that of ferrocene molecule. Since the real and chemical free energies of hydration of ferrocene molecule are the same (as it is uncharged) these cancel and the difference between the real and chemical free energies of hydration of the ion can be obtained. It corresponded to $\chi^{H_2O} = -0.3 \pm 0.1$ V. The two major sources of uncertainty in this calculation are the chemical free energy of hydration of Fec$^+$ and the gas phase ionisation potential of ferrocene, which enter into the calculation as follows:

$$F\chi^{H_2O} = \text{(reliably known quantities)} - \Delta\mu^{H_2O}_{Fec^+} - {}_0 9_1$$

The value given for the electrical part of $\Delta\mu^{H_2O}_{Fec^+}$ is -42.7 ± 2.2 kcal. If the ion were spherical and the ionic radius correct the Born equation would probably overestimate $-\Delta^{H_2O}_{Fec^+}$ which would mean that the true value of $\chi^{H_2O}_{Fec}$ would be more negative than that found. The ion is in fact not spherical[108] and it is difficult to judge in what way $-\Delta\mu^{H_2O}_{Fec^+}$ may be in error. The ionisation energy is a much larger quantity, ${}_0 9_1 = 162 \pm 2.3$ k cal. The energy of ionisation required is the "adiabatic" value, whereas that which is measured[109] is for a "vertical" transition (i.e. without change of nuclear configuration as required by the Franck–Condon principle). The measured value can be equal to, or more probably higher than, the adiabatic value. If it is higher then the true value of χ^{H_2O} should be more positive than that found. If the adiabatic ${}_0 9_1$ were 5% (8 k cal) lower than the value used, then the true χ^{H_2O} would be positive.

From all the work surveyed in this section I do not think that a more precise conclusion can be reached than that χ^{H_2O} lies between $+0.3$ V and -0.4 V. This is equivalent to an uncertainty of ± 8 k cal mol^{-1} in the values of single-ion "chemical" hydration energies. Despite this uncertainty there is a bias in favour of χ^{H_2O} being negative. Other methods of estimating χ^{H_2O} based on its temperature dependence point to χ^{H_2O} being positive and the arguments in this direction appear to be more compelling. These methods are discussed in the next section.

4.2 Estimation of χ^{H_2O} from $d\chi^{H_2O}/dT$

The first serious attempt to estimate χ^{H_2O} on other grounds than those discussed above was made by Frumkin, Jofa and Gerovich.[92] They reached the conclusion that χ^{H_2O} is small and positive, probably $+0.1$ to $+0.2$ V. One argument, based on the change of surface potential caused by the adsorption of organic molecules at the surface, was later elaborated by Frumkin[74] but the evidence is rather indirect and I shall not discuss it here. Of more importance was the argument based on the temperature coefficient of surface potentials. The E.M.F. of the cell (using aqueous solutions)

$$\begin{array}{l|c|c|c|}
\text{Hg HgCl, 1 M KCl} & \text{0.01 M KCl} & \text{Air} & \text{0.01 M KCl} \\
\quad T_0 & T_0 & \Delta\psi = 0 & T_1
\end{array}$$

$$\begin{array}{c|l}
\text{0.01 M KCl} & \text{1.0 M KCl, HgCl Hg} \\
T_0 & \quad T_0
\end{array}$$

was measured for different values of the temperature T_1, T_0 being constant. If the potential difference due to the temperature change from T_1 to T_0 in the 0.01 M KCl solution can be neglected, as there is evidence that it can,[110] then $d\chi/dT_1 = dE/dT_1$. Here χ is the surface potential of the 0.01 M KCl solution, which is not significantly different from χ^{H_2O}. For the cell shown dE/dT_1 was found to be negative and the temperature dependence of E could be expressed by the equation

$$E = \frac{a}{T_1} - \text{constant} = \frac{a}{T_1} - \frac{a}{T_0} \tag{54}$$

with $a = 24$ V deg^{-1}.

It is not difficult to see that a dependence of χ on T compatible with Eq. (54) is theoretically reasonable. A single layer of water molecules with their dipoles all parallel and at right angles to the plane of the layer would produce a potential difference of several volts across the layer. The actual surface potential of water is almost certainly a small fraction of this and so requires only a small bias in the average orientation of water molecules in the surface zone. Such a bias implies a dependence of the average potential energy of a molecule in this zone on its orientation relative to the surface. A reasonable expression for this dependence would be

$$\Delta\bar{u} = \bar{u} - \bar{\bar{u}} = \Delta u \cos\theta \tag{55}$$

where $\bar{u}$ is the average potential energy of a molecule whose dipolar axis makes an angle θ with the normal to the surface (z), and $\bar{\bar{u}}$ is the average potential energy for a molecule for which $\theta = \pi/2$; Δu is a constant. The component along z of the dipole μ of a molecule at angle θ is $\mu \cos\theta$. Using a Boltzmann distribution based on (55), a calculation identical with that used to determine the average polarisation of a molecular dielectric in a field, shows that if $\Delta u < kT$

$$\bar{\mu} = \frac{\Delta\mu}{3kT}\cdot\mu \tag{56}$$

where $\bar{\mu}$ is the average component along z of each molecular dipole. Since $\chi^{H_2O} \propto \bar{\mu}$ it follows, if Δu is constant†, that $\chi^{H_2O} \propto T^{-1}$. This confirms that the

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† In fact, Δu would be expected to decrease as the surface zone becomes more diffuse with rise of temperature. This being so, if $\chi^{H_2O} \propto T^{-n}$, we would expect n to be rather larger than unity.

relation implied by Eq. (54), i.e.

$$\chi\frac{\mathrm{H_2O}}{T} = \frac{a}{T} \tag{57}$$

is a reasonable one.

For water, since $a = 24$ V K, Eq. (57) leads to

$$\chi^{\mathrm{H_2O}}_{298} = 0.081\ \mathrm{V}; \left(\frac{\mathrm{d}\chi^{\mathrm{H_2O}}}{\mathrm{d}T}\right)_{298} = -0.27 \times 10^{-3}\ \mathrm{V\,K^{-1}} \tag{58}$$

Similar measurements, using 0.01 M NH_4NO_3 in ethanol, and the same electrodes, gave $a = -89$ VK whence $\chi^{\mathrm{EtOH}}_{298} = -0.30$ V and $(\mathrm{d}\chi^{\mathrm{EtOH}}/\mathrm{d}T)_{298} = +1.0 \times 10^{-3}\ \mathrm{V\,K^{-1}}$. The directly measured E.M.F. of the cell

$$\begin{array}{c|c|c|c|c} \text{Hg HgCl, 1 M KCl} & \text{0.01 M HCl} & \text{Air} & \text{0.01 M HCl} & \text{1 M KCl, HgCl Hg} \\ (\mathrm{H_2O}) & (\text{EtOH}) & \Delta\psi = 0 & (\mathrm{H_2O}) & (\mathrm{H_2O}) \end{array}$$

was 0.378 V. If the two liquid junction potentials are assumed to cancel, then $E = \chi^{\mathrm{H_2O}} - \chi^{\mathrm{EtOH}}$ and this agrees (fortuitously well) with that calculated from the previously given values, 0.38 V.

Obviously in the above work the neglect of thermal, and liquid junction, potentials may be criticised and the validity of Eq. (57) questioned. However, corroboration is to be had from later work. The E.M.F. of the cell

$$\overset{T_0}{\overrightarrow{\begin{array}{c|c|r} \text{Cu} & \text{Ag} & \text{AgCl, KCl(m)} \\ & & (\mathrm{H_2O}) \end{array}}} \left| \begin{array}{c} \text{Air} \\ \Delta\psi = 0 \end{array} \right| \overset{T_1}{\overleftrightarrow{\begin{array}{l|c|c} \text{KCl(m) AgCl} & \text{Ag} & \text{Cu} \\ (\mathrm{H_2O}) & & \end{array}}} \Big| \overset{T_0}{\overleftarrow{\text{Cu}}} \tag{59}$$

was measured[72] for different values of T_1 (T_0 being constant) and for $m = 1.0$, 0.1 and 0.01 mol/Kgm H_2O. Similar measurements were made with 0.05 M.NaOH and 0.05 M.Na_2SO_4. The only thermal gradient in a conductor is in copper and the contribution of this to the measured E.M.F. is certainly small.[111] However, since the temperature of one electrode is varied, the entropy change in the half reaction at this electrode must be known and this requires the knowledge of a single-ion entropy. There is now good evidence[112] that the absolute value of the standard entropy of hydrogen ion in water, $\bar{S}^\circ_{\mathrm{H}^+}$, is -5.3 ± 0.3 cal K^{-1} mol^{-1}. Hence $\bar{S}^\circ_{\mathrm{Cl}^-} = 18.5 \pm 0.3$ cal K^{-1} mol^{-1}. Using this value, $\mathrm{d}\chi/\mathrm{d}T$ was found to be $-0.44 \times 10^{-3}\ \mathrm{V\,K^{-1}}$ for the 0.01 M KCl solution at 298 K, and the corresponding calculation for 0.05 M NaOH gave $-0.42 \times 10^{-3}\ \mathrm{V\,K^{-1}}$. The measurements may equally well be regarded as leading to the "real" standard entropy of a single ion,[111] $\bar{S}^\circ_{\mathrm{R}i}$ where

$$\bar{S}^\circ_{\mathrm{R}i} = \bar{S}^\circ_i - z_i F\,\frac{\mathrm{d}\chi^{\mathrm{H_2O}}}{\mathrm{d}T}$$

The value found[111] for chloride ion was $\bar{S}_{\mathrm{R\,Cl^-}} = 8.6 \pm 0.2$ cal K^{-1} mol^{-1} at 298 K, from which

$$\frac{d\chi^{H_2O}}{dT} = \frac{-(18.5\text{–}8.6)}{F} = -0.43 \pm 0.02 \times 10^{-3}\ \mathrm{V\,K^{-1}}. \tag{60}$$

If we accept Eq. (57) then from (60)

$$\chi_{298}^{H_2O} = +0.13 \pm 0.01\ \mathrm{V} \tag{61}$$

It is certain that Eq. (57), even if valid at room temperature, cannot remain so at high temperatures since χ^{H_2O} must vanish at the critical temperature of water (647 K). If $d\chi/dT$ were constant up to this temperature it would follow that $\chi^{H_2O} = +0.15$ V. Since the magnitude of $d\chi/dT$ probably decreases with increase of temperature the lower estimate (Eq. 61) is more probable. Another possible line of argument would be to assume that χ should be related to $d\chi/dT$ as the dielectric constant of water ε is to $d\varepsilon/dT$. This leads to the result $\chi^{H_2O} = +0.095$ V at 298 K.

Comparison with other solvents yield some further evidence. Case and Parsons[113] have measured the E.M.F. of cells of the type

$$\mathrm{Ag{\cdot}AgCl\ NaCl(H_2O)}\left|\begin{array}{c} N_2 \\ \Delta\psi = 0 \end{array}\right|\mathrm{NaCl(S)\ AgCl{\cdot}Ag}$$

where S is a solvent such as methanol, ethanol etc. From the measurements the difference between real free energies of solvation of ions in water and the solvent were calculated. For hydrogen ion

$$\alpha_{H^+}^{MeOH} - \alpha_{H^+}^{H_2O} = -5.8\ \mathrm{k\ cal\ mol^{-1}} \tag{62}$$

The free energy of transfer of electrolytes from water to methanol have been studied[114,115] and, by graphical extrapolation methods, subdivided into single-ion "chemical" free energies of transfer. Thus

$$\Delta\mu_{H^-}^{\circ(MeOH)} - \Delta\mu_{H^+}^{\circ(H_2O)} = \begin{array}{l} -2.5\ \mathrm{k\ cal\ mol^{-1}}\ (\text{Ref. } 114) \\ -1.97 \pm 0.35\ \mathrm{k\ cal\ mol^{-1}}\ (\text{Ref. } 115) \end{array}$$

Taking the figure -2.1 ± 0.5 k cal mol^{-1}, together with Eq. (62) gives

$$\chi^{MeOH} - \chi^{H_2O} = -0.16 \pm 0.02\ \mathrm{V}$$

Case and Parsons[113] also examined carefully the change of real solvation energies of ions in methanol–water mixtures, with change of solvent composition from pure water to pure methanol. By a rather convincing argument they concluded that

$$\chi^{MeOH} - \chi^{H_2O} = -0.31\ \mathrm{V}$$

and from the reasoning used it seems that the error should not exceed $\pm$ 0.05 V. From these results we may estimate that

$$\chi^{\mathrm{MeOH}} - \chi^{\mathrm{H_2O}} = -0.28 \pm 0.05 \text{ V} \tag{63}$$

The temperature coefficient of χ^{MeOH} has been measured[116] relative to that for water, with the result

$$\frac{\mathrm{d}\chi^{\mathrm{MeOH}}}{\mathrm{d}T} = +1.85 \times 10^{-3} \text{ V K}^{-1} \tag{64}$$

If the simplest assumption is made, i.e. that

$$\frac{\chi^{\mathrm{H_2O}}}{\chi^{\mathrm{MeOH}}} = \frac{\mathrm{d}\chi^{\mathrm{H_2O}}/\mathrm{d}T}{\mathrm{d}\chi^{\mathrm{MeOH}}/\mathrm{d}T} \tag{65}$$

then using the figures given in Eqs. (60), (63) and (64), we deduce

$$\chi^{\mathrm{H_2O}} = +0.05 \text{ V}\,;\ \chi^{\mathrm{MeOH}} = -0.23 \text{ V} \tag{66}$$

Values of $\mathrm{d}\chi/\mathrm{d}T$ with χ as derived by equation (57), for EtOH, MeOH and H_2O are summarised in Table VI.

TABLE VI

		$\mathrm{d}\chi/\mathrm{d}T$	χ
EtOH	$a = -89$ V K	1.0×10^{-3} V K^{-1}	-0.30 V
MeOH		1.85×10^{-3} V K	-0.23 V
H_2O	$a = +24$ V K	-0.27×10^{-3} V K^{-1}	$+0.08$ V
		-0.43×10^{-3} V K^{-1}	$+0.13$ V

The collected data, although obviously subject to uncertainty, are self-consistent with respect to sign and approximate magnitudes. If $\chi^{\mathrm{H_2O}}$ were really negative this self-consistency would be lost. The relative magnitudes of χ for the three liquids conform to the conclusion at the end of Section 1.2 that additional structure at the surface of these liquids decreases in the order EtOH > MeOH > H_2O. We may also recall that the surface potential changes produced by large cations and anions, discussed in Section 3.5, gave mild support to a positive value for $\chi^{\mathrm{H_2O}}$.

In addition to the experimental approaches, one careful attempt has been made[117] to calculate the preferred orientation of water molecules in the liquid–vapour transition zone, using the dipole and quadrupole moments of the water molecule. Calculations for temperatures not greatly below the critical temperature indicated a preferred orientation with the protons directed towards the liquid phase. An extrapolation to 298 K gave the very tentative estimate:

$$\chi_{298}^{H_2O} = +0.029 \text{ V}$$

which was thought to be "probably an underestimate" but should certainly have the correct sign.

The results discussed in this section are collected in Table VII.

TABLE VII

χ^{H_2O}	Source
$+0.081$ V	Eq. (57) with $d\chi^{H_2O}/dT$ from Ref. 92
$+0.13$ V	Eq. (57) with $d\chi^{H_2O}/dT$ from Ref. 72
$+0.095$ V	analogy with dielectric behaviour, $d\chi^{H_2O}/dT$ from Ref. 00
$+0.05$ V	Eq. (65) with data from Refs. 113, 116 and 72.
$> +0.029$ V	theoretical, from Ref. 117.

These figures can be summarised in the statement $0.03 < \chi^{H_2O} < 0.13$ V.

4.3 Conclusions

The values of χ^{H_2O} derived from the "real" and "chemical" free energies of hydration of ions, by the methods discussed in Section 4.1, varied considerably. In summarising those results I suggested that they did not justify a statement about χ^{H_2O} more precise than $-0.4 < \chi^{H_2O} < +0.3$ V, although there was a definite bias towards a negative value. The results discussed in Section 4.2 point to a value of χ^{H_2O} lying between $+0.03$ and $+0.13$ V. My own view is that greater weight should be given to this estimate of χ^{H_2O} and I would conclude that

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

If this is accepted then the contribution that the surface makes to $\alpha_{+}^{H_2O}$ is $+1.8 \pm 1.4$ k cal mol^{-1}. Hence the "chemical" free energy of hydration of the proton is

$$\Delta\mu_{H^+}^{oH_2O} = -260.5 \pm 0.5 - (1.8 \pm 1.4) \text{ k cal mol}^{-1}$$

or finally

$$\Delta\mu_{H^+}^{oH_2O} = -262.3 \pm 1.6 \text{ k cal mol}^{-1}.$$

Symbols list

a	molecular surface area defined by equation (18)
a_i	activity of ion i
e_0	charge of proton
$g^{\sigma e}$	molecular surface excess free energy (Eq. 20)

k	Boltzmann's constant
m	molal concentration of a solute
n'	number of adsorbed anions per cm^2 of surface
q'_-	charge due to adsorbed ions per cm^2 of surface
r_i	ionic radius
$s^{\sigma e}$	molecular surface excess entropy (Eq. 19)
$u^{\sigma e}$	molecular surface excess energy (Eq. 21)
v_i	partial molar volume of component i of a solution
v_m	molar volume of a pure liquid
v_0	constant in equation (24)
y	number of monolayers of water equivalent to surface excess of water
z_i	electrovalency of ion i
A	area of phase σ
E	E.M.F.
F	Faraday constant
$^{\sigma}$	Free energy of phase σ defined by Eq. (9)
G^{σ}	Free energy of phase σ defined by Eq. (10)
K	degrees Kelvin
N_A	Avogadro's number
N_i^{σ}	number of molecules of component i in phase σ
P	pressure
R	molar gas constant
S^{σ}	Entropy of phase σ
T_c	Critical temperature of a fluid
U^{σ}	Internal energy of phase σ
$V\sigma$	Volume of phase σ
$\alpha_i^{H_2O}$	real free energy of hydration of ion i
γ	surface tension
γ_i	activity coefficient of ion i
$\Gamma_{i(j)}$	thermodynamic surface excess of component i relative to component j
ε	dielectric constant
λ	average intermolecular distance between nearest neighbours in the bulk liquid
μ_i	molecular chemical potential of component i
$\Delta\mu_i^{H_2O}$	"chemical" free energy of hydration of ion i
ν	number of ions derived from one molecule of electrolyte
ρ	local density (time-average)
τ	thickness of phase σ
ϕ	molal osmotic coefficient (Eq. 38)
ϕ^A	Galvani (inner) potential of phase A
χ^A	surface potential of phase A

ψ^A	Volta (outer) potential of phase A
ω	Pitzer's acentric factor (Eq. 22)

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Discussion of the Paper by J. E. B. Randles

R. Parsons I would like to mention that Dr. B. Case and I[1] measured the change or real potential of Cl^- between H_2O and D_2O in one experiment. From Swain and Bader's[2] estimate of the solvation energy difference in these two solvents, this leads to the result that the surface potential χ is 7 mV more positive in D_2O than in H_2O. If one assumes that D_2O is more structured than H_2O and hence behaves as water at a lower temperature, this value supports Randle's value for the temperature coefficient of χ.

I wonder if some clue about the orientation of H_3O^+ suggested by Randles might be obtained from the temperature coefficient of χ.

I think that it is interesting to note that there seem to be no anomalous behaviour of H_3O^+ at the mercury–water interface.

In the comparison of PF_6^- and R_4N^+ ions it would obviously be interesting to study perfluorinated tetraalkyl ammonium ions. I do not think this has been done, but it may be worth noting that in the study of insoluble films, perfluorinated long chain alcohols have unusually large surface potentials.[3]

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J. E. Mayer Professor Randles did not mention the agreement between two different conclusions which he had drawn, namely that of the sign of the surface potential of pure water and that of the difference in surface tension increment for salts and the corresponding acids. In the latter case he concluded that the surface H_3O^+ ions were oriented with the protons directed downward into the bulk water. A positive value of the surface potential of pure water implies a preferred orientation of H_2O, with the protons directed toward the bulk water. It is obvious to assume that in both cases of H_3O^+ and H_2O, whatever preference there is in orientation, it would be the same.

There is one other question, however, with regard to the explanation of the difference between salts and the corresponding acids. Is it not possible that the difference is essentially due to the presence of undissociated acid in the surface layer with the dipole orientation positive end down?

J. E. B. Randles First, with regard to the D_2O, H_2O comparison pointed out by Dr. Parsons, it certainly seems to fit in a very nice way with what I said. I wonder if there is anything that could be said from the theoretical point of view about probable preferred orientation in the surface, on the lines of the paper by Stillinger and Ben-Naim. Is there any possible reason for thinking that one may predict that D_2O will be more orientated in the surface than is H_2O? It looks in fact from what Dr. Parsons says as though it is simply an aspect of the general fact that D_2O behaves as H_2O at lower temperatures.

A. R. Ubbelohde In deuterium oxide D_2O as compared with water, do the shifts of characteristic temperatures such as the freezing point T_f, and the temperature of maximum density $T_{max.}$ change in the same direction, even if numerically the difference (D_2O–H_2O) is not the same? And does this also apply to differences in the surface properties of D_2O compared with H_2O? Have systematic theories of isotope effects in surface properties been put forward?

J. E. B. Randles I was just thinking what 10 mV represent in terms of the difference in temperature; I think it would be about 15°C. D_2O will then have the same surface potential as water would have, at 15°C lower.

In reply to Prof. Mayer, the orientation of H_3O^+ seems to be similar to the H_2O orientation and fit in quite well. As to this question about the effect of acids giving ion pairs or even undissociated acid molecules which are orientated at the surface layer: HCl shows definite evidence of being present as undissociated molecules in the surface layer, from surface tension measurements at high concentrations. But there is certainly no evidence of this for $HClO_4$ or HPF_6 which are very strong acids. I think that, because in that case also the difference in surface potential between the acid and the salt is just conspicuous, it must be a property of the dissociated acid and not of undissociated ion pairs.

I think the suggestion of Dr. Parsons that one should measure the temperature coefficient of the surface potential for acids might be useful. One would have to subtract the effect of the temperature coefficient of the diffuse double layer, but this could be done.

H. G. Hertz

1) It may be of interest that two of the ions which are strongly adsorbed on the interface, PF_6^- and ClO_4^-, produce a splitting of the OH valence vibration band of the solvent DOH in the IR and Raman spectrum. There is a small number of other ions which cause the same effect, e.g. BF_4^-. It is not known yet how to explain this particular behaviour of vibration spectra. It is not correct to ascribe the splitting to the structure breaking effect in general.

Furthermore, the anions ClO_4^-, PF_6^-, and BF_4^- cause an abnormal increase of the nuclear magnetic relaxation rate of ^{23}Na in the centre of the Na^+ ion in the corresponding aqueous solutions. ^{23}Na relaxes by quadrupole interaction and one can conclude that there must be some particular arrangement of water molecules in the hydration layer of these anions. Perhaps it is worthwhile to look further into the interrelations between these three properties.

2) As concerns the question of the orientation of water molecules at the water–gas interface, some experimental results are of interest, which yield information regarding the orientation of H_2O molecules in the hydrophobic hydration layer. There is certainly some similarity between the interfaces air–water and inert group–water.

In order to demonstrate these results, it is useful to begin with the hydrated sphere of the F^- ion. The study of the nuclear magnetic relaxation rate of ^{19}F in aqueous F^- solutions and the comparison of the relaxation rates of ^{19}F in D_2O, D_2O^{17}, and HDO solutions clearly show that one OH proton of water is strongly directed towards the centre of the ion, i.e. the asymetric orientation of the water molecules in the F^- hydration sphere is the correct one. However if one studies the proton relaxation in the solutions

a) $DOOCCD_2CD_2H$, D_2O
b) $DOOCCD_2CD_2H$, D_2O^{17}
c) $DOOCCD_2CD_2H$, HDO

one finds that the interaction with the O^{17} nucleus is stronger (when normalized to the same magnetic moment) than that with the proton. Thus here the orientation of the water molecule in the hydrophobic hydration of the methyl group is such that the protons point away from the CH_3. This is in agreement with the orientation assumed for the water–gas interface.

J. E. B. Randles I have just one comment with respect to the second point Prof. Hertz brought up.

Can we distinguish between the water molecules directed symmetrically with the oxygen towards the proton as distinct from being directed with one negative lobe towards the proton?

H. G. Hertz The only thing we can say so far is that the water protons are further away from the CH_3 protons than the oxygen nucleus. A more detailed theoretical evaluation has to be done.

D. H. Everett Prof. Hertz's direct confirmation of the orientation of a water molecule close to a negative fluoride ion is of considerable importance because it provides support for the electrostatic model adopted for the water molecule in many early calculations such as those I mentioned previously. I would like to ask Hertz whether there is any possibility of devising ways of making similar studies on larger anions? I ask this particularly since if one calculates the potential of a water molecule close to a negative ion as a function of the orientation of the molecule one obtains a curve such as that shown below. (Fig. 20). The two minima do not coincide with the configuration in which the OH-bond points directly at the centre of the ion, but are displaced by an angle ϕ. For short distances (small ions) $\phi = 0$ but as the distance from the ion increases ϕ increases and at sufficiently large distances the two minima coincide to give a single minimum at $\phi = 52°$: the favoured orientation near a negative ion changes from that in which $\phi = 0$ for a small ion, to $\phi = 52°$ for a large ion. It would be very interesting if this could be checked experimentally.

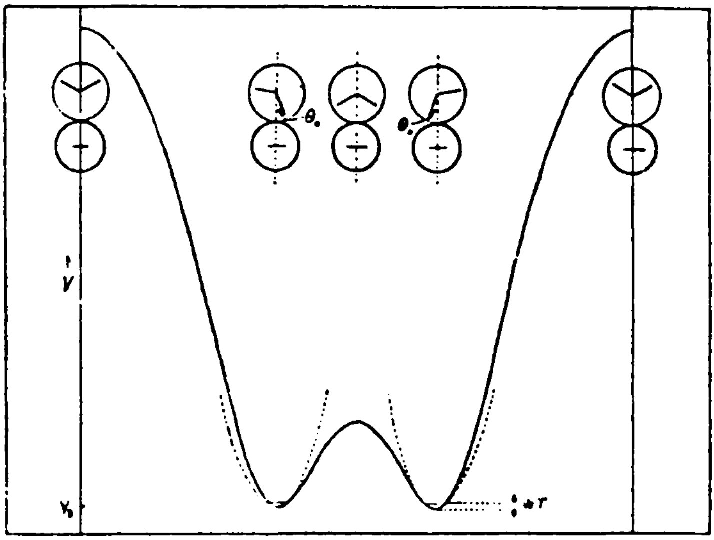

FIGURE 20 P.E. curve for rotation of water molecule in field of cation about axis (c). Dotted curves: P.E. curves for S.H.M.

References

D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, **34**, 1093 (1938).
D. H. Everett and C. A. Coulson, *Trans. Faraday Soc.*, **36**, 633 (1940).

H. G. Hertz For the following reason, the range of possible applications as given for F^- is very limited: most ionic nuclei have spin larger than $\frac{1}{2}$. In this event the nuclei relax by quadrupole interaction. Now the electric field gradient at the nucleus enters, which cannot be used to give the desired information concerning relative particle orientation. But in principle, even in cases where the nuclear spin of the ion exceeds $\frac{1}{2}$, informations can be obtained by more sophisticated methods. Another difficulty arises here when other relaxation mechanisms occur like spin-rotation interaction.

M. L Josien Nous avons appliqué la spectroscopie infra-rouge à l'étude des interactions entre les molécules H_2O, D_2O, HOD d'une part et les sels ou les bases organiques d'autre part (1).

Dans le cas des ions Br^-, l'évolution du spectre de D_2O en solution dans l'acétonitrile montre que, par addition de $BrNBu_4$, on forme successivement des complexes de type 1-1 $DOD \cdots Br^-$, puis de type 1-2, $Br^- \cdots DOD \cdots Br^-$ (1).

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J. E. B. Randles I found just a little surprising that you can have two bromide ions attached to one water molecule. I would have thought that the repulsion function would prevent this.

H. A. Resing Prof. Hertz, does the interatomic distance you have given represent a distance of closed approach in some continuum model of the relaxation time? (Give reference please, Prof. Hertz).[1]

Reference

1. H. G. Hertz and C. Rädle, *Ber. Bunsenges.*, **77**, 521 (1973).

H. G. Hertz There is no model involved in the primary experimental results. One only compares the increase of the proton relaxation rate per added ^{17}O with the increase per added ^{1}H nucleus. Since both nuclei are on the same molecule, the correlation times are the same, thus difference in relaxation rate means difference of closest distance of approach (of course after suitable normalization to the same magnetic moment). In a further step, one may apply a model and obtain more quantitative results.

R. Diamond I would like to comment on the position of PF_6^- in the sequence of ions absorbed in the water surface, and on the similarity of the sequences with water–air and water–mercury interfaces. Although some properties qualify PF_6^- as a structure breaker, we should remember that there is a continuous range of behaviour from the moderate-sized ion that permits rotational freedom for the water next to the ion (structure breakers) to the larger, hydrophobic ions. The PF_6^- ion is somewhere midway, like the NMe_4^+ cation. It is large enough and hydrophobic enough to interfere somewhat with the hydrogen-bonded water network, and so is pushed to the less-structured surface. If we now consider the distribution of ions into less-structured, less hydrogen-bonded phases, such as the extraction of various salts into organic phases or the exchange of anions into a strongly-basic exchange resin, we usually obtain the same order of increasing distribution, for example, $I^- < ClO_4^- < AuCl_4^-$, (and FP_6^- falls, I believe, between ClO_4^- and $AuCl_4^-$). I do not think the data are available, but I would predict that $AuCl_4^-$ would go into the water surface even more strongly than PF_6^-. The similarity in the order for distribution into the water–air interface, the water-mercury interface, the organic solvent phase, and a strongly basic exchange resin, just as for the corresponding sequences with the tetra-alkylammonium cations, indicate that the order comes primarily from the same cause or interactions in the bulk water phase. There may well be, and surely are, differences between cations and anions as classes and between individual ions due to the possibilities of water hydrogen-bonding to anions, to dispersion force interactions, and to preferential orientation of water molecules at the surface, but I believe the increasing non-hydrophilic volume of the sequence of ions and consequent increasing disruption of the bulk-water structure is of primary importance in determining the order of distribution between bulk water and the surface phase.

J. E. B. Randles I would like to ask Prof. Everett, if his rather fully-bonded model does in fact give an explanation why these ions are forced into the interface? I don't feel quite sure that it would, but I would like to know what is your opinion.

D. H. Everett The idea that insertion of an ion or a neutral molecule into the kind of continuous network structure which I have described, leads to the creation of a defect which tends to migrate to the surface, may well be important in determining the adsorption of ions at the liquid interface.

W. Drost-Hansen Professor Randles notes that recent surface tension data on pure water do not appear to reveal thermal anomalies. I agree completely with this statement. However, thermal anomalies exist and I will discuss these in my paper. I do feel that *many* sets of apparent surface tension data suggest anomalies, but, I believe these are manifestations of (induced) structural effects, occuring at the three phase interface: air/water/glass (or quartz) (which may particularly have influenced measurement made in capillaries).

A. Bellemans In addition to the works of Onsager-Samaras and Buff-Stillinger on the surface tension of aqueous electrolyte solutions, I would like to mention some recent theoretical calculations made in collaboration with J. C. Bernard (Thesis 1970, Univ. of Brussels), which are still unpublished. The model used is the so-called primitive model of electrolyte solutions (i.e. a structureless water embedding ions with a spherical hard core) and the water-air interface is treated as a sharp discontinuity. The Mayer-McMillan cluster expansion was first adapted to surface problems and next rearranged in order to cancel the well known divergences arising from the long range coulombic interactions. In this way one gets a systematic *nodal expansion*, each node corresponding to one ion surrounded by a Debye cloud of opposite charges. The lowest term in this expansion involves a single node interacting with its own image and it leads to $\Delta\gamma$ values almost coincident to the Buff-Stillinger treatment (here $\Delta\gamma$ denotes the change of surface tension with respect to pure water). As it is known, these theoretical values are definitely smaller than the experimental ones for alkali halides. It was hoped that the consideration of higher order terms of the nodal expansion would reduce the discrepancy. It is actually the *reverse* which is observed: when the contribution of two nodes is included (i.e. correlation effects between a pair of ions screened by their respective Debye clouds) the disagreement with experiment is further increased!

This clearly demonstrates the very limited applicability of the primitive model of electrolyte solutions to surface tension. Obviously *ad hoc* assumptions can be introduced, involving a thin superficial layer of water with a lower dielectric constant than the bulk; this may force agreement with experiment; however, the physical meaning of the parameters which are introduced is not very clear. It is even very doubtful that an elaborate statistical treatment involving a surface dielectric tensor instead of an isotropic dielectric constant would be of any value. What is really needed is a full statistical theory retaining explicitely the molecular structure of water near the interface.

S. A. Rice Much of the discussion has concerned details of the structure of the surface of water, but all the experimental data cited are thermodynamic in nature. At best these data can only test the consistency of models of the surface and certainly cannot be used to obtain structural information. To make the point more explicit, I note that many of the deductions cited depend on the assumption that the transition zone from bulk liquid to vapour can be characterized by a monotonic change of density with distance. But recent calculations[1] indicate that the transition zone between a dielectric liquid and its vapour, or a window, likely has a peak in the density profile, and may even have density oscillations. Experimental studies of liquid Hg[2] and of Hg–In alloys[3] are consistent with the existence of a peak in the conductivity in the transition zone between liquid and vapour or window. There is also evidence that the transition zone is somewhat different at liquid-vacuum and liquid-dielectric window interfaces. Clearly, we must be wary of structural information derived entirely from thermodynamic measurements.

The preceding remarks are cast in a negative tone. To take the positive view we ask how information about the structure of the surface of water can be obtained. I suggest that the combination of ellipsometry and reflectance spectroscopy, especially in the region of absorption, will be useful. The region of strong absorption is of importance for two reasons. First, the surface zone is very thin and will have maximal influence on the observed reflectance (or ellipsometry) when the penetration depth of the light is minimal. Second, and perhaps more important, the collective surface vibration spectrum must depend to some extent on the structure of the surface, hence is a probe of that structure.

Although the suggested experiments are superior to thermodynamic measurements, they are not free of ambiguity because they also depend mainly on integrated properties of the surface zone. Nevertheless, they can in principle supply information not now available. Direct determination of surface structure must await improvements in direct diffraction techniques – surely these will be needed before the structure of the surface can be definitively determined.

References

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2. A. N. Bloch and S. A. Rice, *Phys. Rev.*, **185**, 933 (1969).
3. B. Siskind, J. Boiani, and S. A. Rice, *Can. J. Phys.*, **51**, 894 (1973).

R. Parsons There is some Japanese work of two or three years ago on the ellipsometry of water surfaces. They showed that the diffuseness of the surface increased with temperature. (K. Kinosita and H. Yokota, *J. Phys. Soc. Japan*, **20**, 1086 (1965).)

If one assumes that the water near air is very similar to that near mercury, as indicated by a variety of evidence, then it is reasonable to assume that the dielectric constant is of the order of 6. I shall discuss this more after Prof. Reddy's lecture.

A. R. Ubbelohde Is the pushing out of large ions to the surface of aqueous ionic solutions directly correlated with their size, or must special force fields be involved as well? Do large *polyhydrated* cations of transitional metal ions show this effect, for example? With the growth of inorganic chemistry, the range of ions available that have unusual characteristics, such as might help in experimental investigations of our problems, has likewise grown very greatly. There must be anions other than PF_6^- waiting to be called in to help with our problems.

E. Gileadi I feel that some attention should be paid to the composition of the gaseous phase in contact with the solution. Usually, measurements of surface tension and surface potential are made when the solution is in contact with air saturated with water vapours. Thus the interphase really consists of H_2O, N_2, O_2 molecules. Would γ and $\Delta\chi$ be different if air would be replaced by, say helium and if water vapours were excluded from the interphase?

Could the solubility of the various gaseous species affect the magnitude of the interfacial quantities measured?

Further one wonders if the special behaviour of acids and of the PF_6^- ion at the interphase, mentioned by Prof. Randles, could not be associated with hydrogen bond formation or some other specific interaction with H_2O and O_2 molecules in the gas phase in contact with solution.

J. E. B. Randles In reply to Dr. Gileadi, I think it is true to say that in the past, many surface tension measurements were made both against water vapour as gas phase, and water vapour + argon or nitrogen, and there is no detectable difference. I think really the gas phase plays a very little part.

R. Parsons It is of course possible to get adsorption of gases on water surface in evidence cases, for example, benzene as shown by Jones and Ottewill (*J. Chem. Soc.*, 4076 (1965)).

H. D. Hurwitz I am wondering about the similarities of the behaviour observed at air-water and Hg-water interface since the dielectric environment on the non-aqueous side is totally different.

A. R. Ubbelohde I am struck by the close analogies claimed by some members of the conference between water/gas interfaces and water/mercury interfaces. Does this mean that the metallic conduction in mercury contributes only very little at the interface with water, despite the large electrostatic forces in aqueous ionic solutions? At first sight this seems rather surprising.

One can turn to interfaces between water molecules and other conducting condensed states of matter, to look for possible analogies with mercury. Does liquid gallium show behaviour with aqueous ionic solutions, resembling that to mercury?

J. E. B. Randles It seems to me that at the water/mercury interface, one would not expect a decrease in the water density, as one does at the water/vapour interface.

What I wish to say is that the similarities, in particular with respect to the out-squeezing of the large anions which seems to occur at both interfaces, do seem to imply some structural similarity. There is evidence, of course, for low dielectric constant behaviour of the water layer adjacent to mercury. I believe this is not a matter of decreasing density. I suspect that mercury has some type of interaction with the water molecule, which impedes the rotation of the molecule. It also has some directing effect, I think.

S. A. Rice The transition zones between liquid and vapour and liquid and metal-electrode should have roughly the same structure, although they must certainly differ to some extent. What is most important is to recognize that an interface between a liquid and anything else is inhomogeneous, and certainly never a discontinuity in density such as a geometric plane. It is also important to distinguish between static features of the structure, e.g. the locations of the centres of mass and orientations of the molecules, and dynamic features of the structure, e.g. the vibrational spectrum, rotational autocorrelation function, and so forth. Probably it is the dynamic properties of surface transition zones that are most sensitive to what the liquid is in contact with.

R. Parsons It is possible to measure without assumptions the difference in the real potential of water (or other solvent) and the corresponding dipole potential at the uncharged electrode–solvent potential interface. In the case of Hg-water the potential difference is here -0.26 V at 25°C from Randles measurements. If it is assumed that there is no contribution from the metal itself, this result implies that the orientation of H_2O with the O towards the Hg is greater than the orientation of water with O towards the air at the air–water interface. This is in agreement with the temperature coefficients of these dipole potentials, following Randles interpretation.

J. E. B. Randles Agrees with Parsons.

D. H. Everett Evidence for the change of water structure near a solid hydrophobic surface comes from the measurements of Ash and Findenegg[1] of the volume change accompanying the immersion of graphitised carbon black in water. The expansion observed may be interpreted as a negative adsorption of water molecules at the surface of about 3×10^{-9} gcm^{-2}. The molecular interpretation to be placed on this depends on the assumptions one makes about the properties of the surface layer. For example, if the surface layer is supposed to have the same density as ice then one layer of "icelike" structure is sufficient to account for this effect. Correspondingly if the average density change in the surface region were 1‰, then ten layers would be needed. It is interesting to note that in the case of liquid *n*-alkanes, there again seems to be a somewhat "solid-like" structure near the surface, but this now has a higher density than the liquid and positive adsorption is observed.

Reference

1. S. G. Ash and G. H. Findenegg, *Special Disc. Faraday Soc.*, **1**, 105 (1970).

I do not suggest that the surface layer of water is necessarily "ice-like," but only give that as one extreme of a range of possibilities which depend on how the local density varies near the surface.

H. A. Resing In regard to Prof. Everett's hypothesis of an increased density or "structured" layer of water on a carbon surface, we have found from nuclear magnetic resonance relaxation measurements that the mean mobility of water adsorbed to saturation in charcoal capillaries is about equal to that for bulk liquid water, and this lends no credence to a hypothesis of increased "rigidity" in the first layer.

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H. A. Resing, J. K. Thompson, J. J. Krebs, *J. Phys. Chem.*, **68**, 1621 (1964).
H. A. Resing, Adv. in Molecular Relaxation Processes, 3, 199 (1972).

A. K. N. Reddy The extent of similarity between adsorption at the air-solution and mercury-solution interfaces shown by Randles indicate that, of the three classes of interactions, viz., air/Hg-ion, air/Hg-water and ion-water, the last mentioned is the dominant one.

S. A. Rice The structure of the transition zone between a liquid and a metal (or anything else for that matter) depends on the nature of the molecular interactions. In turn, the interaction that determines a given phenomenon depends on the characteristic frequency spectrum of the phenomenon. The easiest way to see this is to use the representation of intermolecular forces in terms of the frequency dependence of the dielectric function developed by Lifschitz and others (Landau, L. and Lifschitz, E., *Electrodynamics*).

Consider, for example, the case of Hg. The imaginary part of the dielectric function is related to the conductivity and the real part to the polarizability of the ions. Both of these are frequency dependent. At high enough frequencies the conductivity of Hg, like that of other metals, decreases by an order of magnitude from the dc value. There are also (in principle) resonances in the polarizability. Actually, in the case of a metal these resonances appear as band-to-band transitions. In a liquid metal the electron–electron interaction leads to transfers of oscillator strength between hypothetical one electron excitations, the net result being that the conductivity of liquid Hg falls off to a small value long before the simple Drude theory predicted fall off.

Now the thermodynamic properties of the liquid/metal interface presumably refer to a zero frequency response of the system. On the other hand, the dynamical properties of the liquid/metal interface refer to a response at a given frequency, or range of frequencies. It is possible, then, for static and dynamic properties of the surface zone between a liquid and a metal to reflect different effective interactions.

In the case of Hg the conductivity falls dramatically over the energy range 2–4 eV, i.e. in the vicinity of 10^{15} Hz, hence all but the fastest molecular motions "see" the interaction corresponding to the dc conductivity. It is conceivable that there is a high frequency component of the brownian motion of an ion in the liquid near the surface that might sample a different frequency range, but this seems unlikely to be important. On the other hand some semiconductors have important resonances in their dielectric functions for much smaller frequency, and for these there may be measurable differences between the dynamic and static effective interactions in the surface zone on the time scale of, say vibrational motion.

The preceding remarks also apply to the case of liquid–dielectric interfaces.

R. Parsons The extensive work of Frumkin *et al.* on Ga electrodes[1] has shown that water is much more strongly adsorbed at Ga than at Hg. For example organic compounds are more weakly adsorbed at Ga than at Hg.

Thus Ga is a hydrophilic surface while Hg is hydrophobic.

References

1. V. A. Kir'yanov, V. S. Krylov and N. B. Grigor'ev, *Sov. Electrochem.*, 4, 361 (1968); E. V. Osipova, N. A. Shurmovskaya and R. Kh. Burstein, *Sov. Electrochem.*, 5, 1075 (1969).

B. Behr While considering the factors which cause adsorption of ions at interfaces one has to take into account the possible contribution of the polarizability of the ion. Assuming the surface potential of water as equal to 0.08 V and the thickness of the transition layer ca. 8 Å the electric field should be ca. 10^6 V/cm. This can produce induced dipole moments of easily polarizable ions, which may result in somewhat stronger adsorption of I^- or SCN^- ions at H_2O/air interface as compared with less polarizable ions of similar size and charge.

R. Diamond The tetra-alkylammonium cations do not have a very large electron density and so should not be very polarizable. It would seem to me difficult to explain the rather large differences in their behaviour on such grounds. Similarly, PF_6^- must not have a very large surface density of electronic charge, and so should also be not too polarizable. But just because of their difference in charge, anions are more polarizable and do have larger dispersion force interactions than cations, and this may contribute to some of the differences about which we are hearing. Certainly large complex anions containing atoms of high atomic number, such as $AuCl_4^-$ and $AuBr_4^-$, and ions containing double and triple bonds, such as SCN^- may show effects of polarization and dispersion force interactions. But judging again from the distribution order from an aqueous phase into an ion-exchange resin phase, preferential polarizability in either phase does not seem to be the main factor, although it must contribute in some cases.

M. Mandel It may be useful to come back to the concept of dielectric constant in the surface layers. In recent years there has been much theoretical effort to prove that such an intensive quantity, independent of volume and shape as the dielectric constant can be defined. And indeed for ordinary systems it may be shown by a statistical mechanical analysis that the concept of dielectric constant can be justified. I wonder however if the same analysis would apply to a surface layer. If not it might be better not to use the dielectric constant in this layer in order to explain adsorption phenomena, but refer to local polarization.

H. D. Hurwitz We have found at the interface of Hg–aqueous KCl–KF solution that the partial molar excess entropy of water in the adsorbed layer behaves as in the case of an ideal mixture of adsorbed Cl^- and water.

E. Gileadi Considering Prof. Mandel's remark on the meaning of the dielectric constant at the interphase, I feel that in a region one water molecule thick this quantity becomes more of a parameter than a quantity which can be given a sound theoretical basis. It is clear that the bulk dielectric constant of water has little bearing on phenomena at the electrode–solution interphase because of the special structure of water at the interphase. A value of $D \sim 6$ has been found by many authors to fit best the observed capacitance/potential behaviour of the mercury/water interphase.

C. P. Bean I should like to call attention to an application of the Wagner surface ion exclusion effect. As Prof. Randles indicated this simple model of exclusion is based on the fact that ions prefer to enjoy the high dielectric of the bulk rather than have their electric field extended to any large degree into the unit dielectric constant of air. As is well-known, membranes exist that are permeable to water but not to dissolved salts. It is perhaps not so well known that these semi-permeable membranes can be used to purify saline water by ultrafiltration or reverse osmosis. Several generic models exist to explain this phenomenon, and to guide the efforts of membrane synthesis. The Wagner surface ion exclusion effect provides a mechanism by which ion rejection can be understood to occur in a membrane that consists of a medium of dielectric constant ε pierced by macroscopic neutral, cylindrical pores of diameter D.

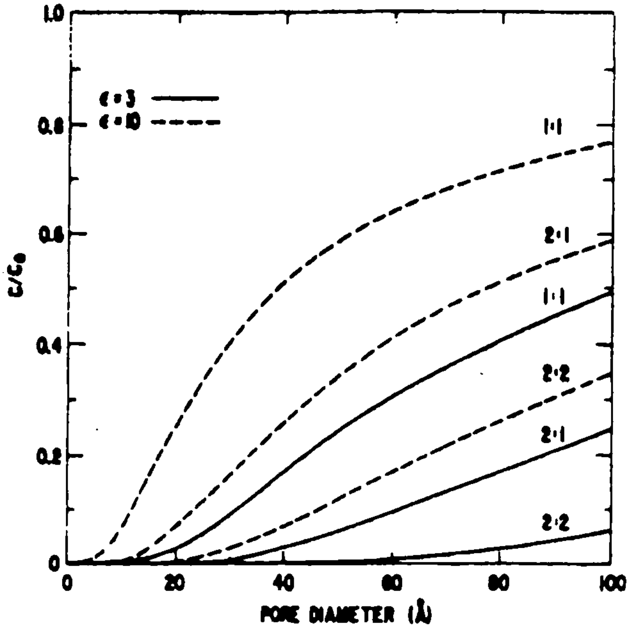

FIGURE IV.2 Plot of the relative concentration within a neutral pore for dilute salt solutions at 25°C. The dashed curves are for a matrix dielectric constant of 10 while the solid ones assume a matrix dielectric constant of 3. The symbols besides each curve indicate the degree of ionization of the ionic components. These curves represent lower limits since the relevant energies are calculated on the axis of the pore and steric effects are neglected.

The basic idea is one of some venerability. Indeed A. Fick's pioneering diffusion measurements were aimed at testing this hypothesis. In recent years E. Clueckauf[1] has made a quantitative essay at a theory while a more accurate attempt[2] has been made possible by the numerical calculations of A. Parsegian.[3] These latter calculations are the analogues of Wagner's image charge theory and can be used together with a Boltzman distribution to calculate, in the limit of extreme dilution, the concentration on the axis of the pore. (This latter restriction arises from the special case of Parsegian's calculation). Figure IV.2 gives results for various salts, dielectric constants and pore diameters. It is worthy of note that pores as large as 100 Å have significant effect. Figure IV.3 presents the course of rejection (defined as I – input concentration/output concentration) as a function of applied pressure in a reverse osmosis configuration calculated on the basis of this theory together with that of diffusion in a moving system. Data on cellulose acetate are included as a general comparison.

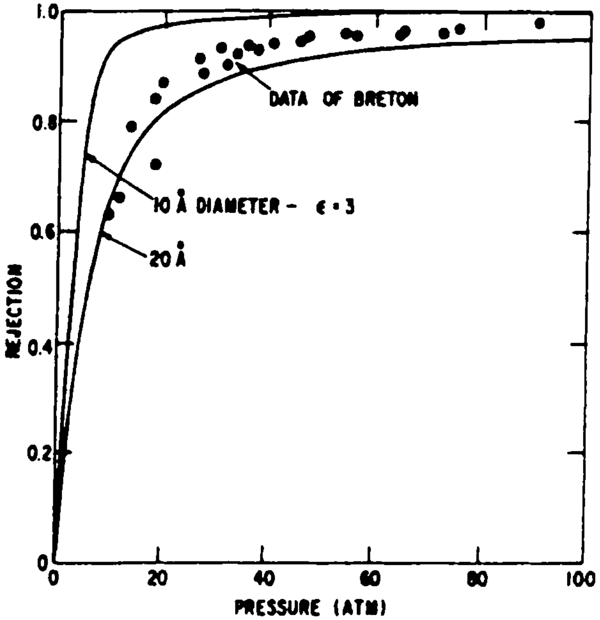

FIGURE IV.3 Theoretical plot of the course of rejection as a function of pressure for 0.1 N NaCl for pore sizes of 10 and 20 Å in a matrix of dielectric constant 3. The data of Breton on cellulose acetate plotted for comparison.

References

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2. C. P. Bean, in *Membranes, A Series of Advances* (G. Eisenman, Ed.) Marcel Dekker, N.Y. 1972, p. 1.
3. A. Parsegian, *Nature*, 221, 844 (1969).

A. R. Ubbelohde Am I to understand that the water in the pore is assumed to have a structure that is altered from that of the bulk liquid?

C. P. Bean No. The solution is assumed to have a full dielectric constant of about eighty. In this approach, as in Wagner's, water is treated as structureless, dielectric continuum. As I understand the remarks of Profs. Randles and Bellemans, the inclusion of structural effects would have the effect of accentuating the properties of ionic exclusion and rejection.

R. Parsons I should like to say that the measurement of real potentials of ions in different solvents leads to a useful approach to the problem of "medium effects" which is connected with the problem of pH scales as well as that of potential scales in different solvents. If one makes measurements in a range of mixed solvents, for example alcohol + water, then one has additional information about the surface layer; that is surface tension measurements yield the surface composition. If one assumes that a region of constant surface composition has a constant surface potential, one can deduce the change in the bulk energy (μ) directly from the real potential (χ). This may be reasonably extrapolated to the two pure solvents and hence the change in μ and χ obtained between the two solvents.[1]

In particular it is interesting to consider results of this type calculated for the ferrocene–ferrocinium system.[2] Here we can find the difference of the real potential of ferrocinium minus the chemical potential of the ferrocene which may be regarded as the free energy of putting a point charge in a ferrocene-sized cavity in the solvent. In the methanol/water system, there is initially a rapid drop of this energy, which is clearly predominently a surface effect, followed by a much slower rise which is predominantly a bulk effect. The slope of this is substantially different from that calculated from the Born equation which indicates, here again the inadequacy of this equation, which has been evident for at least 40 years. This emphasizes the inadequacy of the proposal that the ferrocene electrode should be used as a common reference electrode for all solvents.

This approach using information about the surface layers works when one solvent is strongly adsorbed, e.g. in aqueous solutions of alcohols, acetone, glycol, dioxane, etc. However, in solutions of formamide or dimethylsulphoxide in water, the surface layer is more complicated.

References

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2. R. Parsons and B. T. Rubin, *J. C. S. Faraday I*, (in press).