

Hydrophobic and Electrostatic Interactions in Adsorption at Interfaces: Relation to the Nature of Liquid Surfaces

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Electrostatic and hydrophobic interactions of ions near interfaces are examined in relation to the nature and structure of surfaces of liquids, especially that of water.

The superficial excess entropy and energy of liquid surfaces is calculated from surface tension data, and Stefan's ratio is evaluated for several liquid interfaces. Stefan's ratio is related to the ratio of co-ordination number of surface molecules to that for bulk molecules and leads to information on surface structure. Stefan's ratio is *ca.* 0.5 for non-polar liquids but is near 0.1 for H-bonded liquids. The superficial excess entropy is related to the cohesive energy density and to co-ordination in the surface.

Short-range effects in adsorption of ions at air/water interfaces are determined by the structure of the liquid surface and by electrostatic polarization energy near the interface. Based on the Born equation, relations are deduced for ionic adsorption near liquid interfaces.

By studying the adsorption of a series of propylamine perchlorates at the air/water interface and the corresponding surface potential changes, the relative importance of hydrophobic and electrostatic ion-solvent interaction effects was investigated.

Methods for investigating the entropy of water at charged interfaces are discussed and a theory of entropy of water in the double-layer is reviewed.

INTRODUCTION

In adsorption at interfaces involving water, a critical balance often exists between hydrophilic, electrostatic hydration and hydrophobic interactions, depending on the adsorbate and the interface. Hydrophilic interactions depend on the presence of such functional groups as —OH, —NH₂, $\begin{array}{l} \diagup \\ \text{C=O} \\ \diagdown \end{array}$, —COOH,

$\begin{array}{l} | \\ \text{--NH--C=O} \end{array}$, as well as ionic groups which determine electrostatic hydration; hydrophobic interactions are usually more subtle and arise from the reluctance of non-polar molecules or molecular groups to be surrounded by polar H-bonded water due to the H-bond breaking which their presence introduces. Hydrophobic groups hence tend either to become associated, as in the case of side-chains on proteins and polypeptides^{1,2} or in micelle formation, or to escape the water phase by becoming positively adsorbed at the water interface. The

thermodynamics and statistical-mechanics of the hydrophobic interaction effect in solution have been considered by Ben-Naim in various papers.³ The adsorption behavior of solute molecules at water interfaces also requires consideration of the structure of the water interface itself.

Hydrophobic and electrostatic (ionic) interactions are of great importance in determining the surface excess of solute species at the air/water, the water/mineral and water/electrode interfaces. At the air/water interface, they are also of considerable biological interest as they determine the composition of sea and river water interfaces and influence the rates of exchange of biologically significant gases, such as O₂ and CO₂, between the atmosphere and the water phase, especially in the case of hydrophobic organic substances. Negative adsorption of ionic species, which usually occurs at air/water interfaces, can influence the local solubility of dissolving gases in sea-water on account of changed salting-out behavior.⁴ At interfaces which are, or behave as, electrodes, hydrophobic and electrostatic interactions of solute ions with water are important in (a) adsorption behavior of leveling agents and corrosion inhibitors; (b) mechanisms of organic electrode reactions involving hydrophobic intermediates, *e. g.* in hydro-dimerization of acrylonitrile; and (c) structure of the double-layer.

Factors in Ionic Adsorption at Interfaces. General effects

The approach of an ion to an interface can have several effects on the hydration or solvation of the ion:

(a) At a metal or an oxide interface, water may already be intrinsically oriented, *e. g.* as at Hg,^{5,7} Pt,⁶ SiO₂, *etc.* Hence approach of an hydrated ion to the interface will involve co-sphere interaction of the hydration shell of the ion with the hydration layer of the interface; positive or negative free energy changes may accompany such an approach (within 5–10 Å) depending on the relative orientation of water dipoles at the ion and at the surface and the degree of »structure-breaking« or hydrophobic »structure-making« that either the ion or the interface causes in the water.

(b) If the dielectric constant ϵ of the medium beyond the water interface differs from that of water (or the solvent), then the ion will experience an image interaction with the interface due to induction of charges at that interface. If the medium beyond the water interface has ϵ greater than that of water (*e. g.* a metal where $\epsilon \rightarrow \infty$), an *attractive* image interaction arises, leading to positive adsorption. This is opposed by the reluctance of the ion to suffer displacements of its co-ordinating solvent molecules. If the medium beyond the bulk solvent phase is vacuum, air or its vapor, then an image of *like* sign to that of the ion arises and the hydrated ion is repelled from the surface giving a negative surface excess as found with many ions at the air/water interface. In either case, near a metal or at an air/water interface, the extent of hydration of an ion tends to be restricted due to limited accessibility of the solvent to the ion.

(c) Double-layers are set up near the surface if differential adsorption of cations or anions arises¹⁰ due to their different extents of hydration and surface activities.

It is generally found for simple inorganic ions at air/water interfaces, that their adsorption is negative, *i. e.* their surface excess $\Gamma_1 < 0$. For sufficiently

hydrophobic ions, however, *e.g.* alkyl- and aryl-ammonium type ions, or fatty-acid anions, the Γ_1 is positive. The origin of negative adsorption of simple inorganic ions is easy to understand: the surface phase, being 2-dimensional or semi-3-dimensional, provides a region where an ion can only be *partially* hydrated. It is hence, from a free-energy point of view, in a less favorable situation than in the bulk, so that its adsorption is negative. At finite salt concentrations, a further factor arises connected with the asymmetry of the ionic atmosphere imposed by the presence of a surface.^{9,10} The electrostatic theory connected with these effects has been treated by Wagner,⁸ by Onsager and Samaras⁹ in terms of the image interactions, and by Bell and Rangecroft¹⁰ for asymmetrical electrolytes.

It has been realised for a long time, especially by Frumkin¹¹ and his school¹²⁻¹⁶, that there is a close connection between adsorption of ions and molecules in the double-layer at electrodes and in the interphasial region near the interface of water and its vapor or air. Many of the factors which determine adsorption at the air/water interface such as hydrophobicity,⁵⁷ image interactions and hydration effects¹¹ are significant also at metal electrode/solution interfaces, but usually with an increase of complexity of the interactions.

We first consider factor (a) connected with the state of water and other liquid interfaces.

The State of Liquid Surfaces in Relation to their Superficial Excess Energy and Entropy

(i) Stefan's Ratio and the Energy and Entropy of Liquid Interfaces

Some insight into the state of the surface of a liquid in relation to that of its bulk, and hence how the interface may influence the behavior of a hydrated ion in its neighborhood, may be conveniently gained by evaluating the superficial excess energy E_σ and the entropy S_σ from the surface tension γ (viz. the superficial excess free energy G_σ) and its temperature coefficient $-(\delta\gamma/\delta T)_p$. Normally γ and its temperature coefficient are evaluated as G_σ or S_σ per cm^2 . To relate the thermodynamic properties of the surface to molecular properties it is necessary to obtain G_σ , S_σ and E_σ per molecule or mole. This requires an estimate of the number of molecules per cm^2 in the liquid surface and hence implies already some knowledge concerning the structure of the interface. Experimentally, some information on the dielectric profile in the surface region can be obtained from reflectivity parameters¹⁷.

The average number n of molecules per cm^2 cross-section of a liquid can readily be obtained from the density ρ of the fluid as

$$n = \left(\frac{6.02 \times 10^{23}}{M} \rho \right)^{2/3} = 1/A \text{ molecule cm}^{-2} \quad (1)$$

where A is the mean area requirement per molecule and M is the molecular weight. The question arises whether this value of n or A derived from bulk properties will apply to the natural surface of the liquid, *i.e.* will n_σ (the n value for the liquid surface) differ from n on account of the surface forces under examination? Some indication that n_σ will be approximately equal to n follows from the argument given below.

The surface tension of water, 78 dyne cm^{-1} , has the units of a force constant and hence is equivalent to a force constant determining the extra intermolecular interactions that arise in the two-dimensional layer of the liquid surface. For the intermolecular interactions between H-bonded water molecules themselves in the liquid, the force constant is ca. 10^4 dyne cm^{-1} corresponding to the ir. intermolecular frequency of 100–200 cm^{-1} . Thus, it would seem that the residual forces in the liquid surface would be insufficient to change by ca. more than 1% the number density of water molecules in the surface in comparison with that in a lamina cross-section of the bulk. Hence, the number density in the surface will be $\frac{6.02 \times 10^{23} \rho^{2/3}}{18}$ or the area A per molecule will be given by eqn. (1), where ρ is the density of pure water at a given temperature. Average orientation of water molecules in the surface will, however, be different from that (zero) in the bulk. The surface free energy G_σ per molecule is hence

$$G_\sigma = \gamma \left(\frac{18}{6.02 \times 10^{23} \rho} \right)^{2/3} \text{ erg molecule}^{-1} \quad (2)$$

The corresponding superficial excess entropy $\left(\frac{\partial G_\sigma}{\partial T} \right)_\phi$ is given by

$$S_\sigma = - \left(\frac{18}{6.02 \times 10^{23}} \right)^{2/3} \left[\rho^{-2/3} \left(\frac{\partial \gamma}{\partial T} \right)_\phi - \frac{2}{3} \gamma \rho^{-5/3} \left(\frac{\partial \rho}{\partial T} \right)_\phi \right] \text{ erg K}^{-1} \text{ molecule}^{-1} \quad (3)$$

It will be noted that eqn. (3) takes into account not only $(\partial \gamma / \partial T)_\phi$ but also the variation of the number of particles per cm^2 as the temperature is changed, through the terms in $\rho^{-2/3}$ and $\rho^{-5/3} \left(\frac{\partial \rho}{\partial T} \right)_\phi$, so that S_σ can be expressed per molecule in the surface layer.

The state of a liquid surface in relation to the bulk structure may be investigated by calculating (a) Stefan's ratio^{18,19} $E_\sigma / \Delta L_{\text{vap}}$ where $E_\sigma = G_\sigma + TS_\sigma$ and ΔL_{vap} is the energy of vaporization; (b) the superficial excess entropy S_σ and (c) the ratio $S_\sigma / \Delta S_{\text{vap}}$ where ΔS_{vap} is the entropy of vaporization given by $L_{\text{vap}} / T_{\text{vap}}$ (Trouton's »constant«) where T_{vap} is a temperature at which the vaporization energy is measured or derived.

Stefan regarded particles of a liquid that were situated in a surface as »half-way« between the bulk and vapour states so that $E_\sigma / \Delta L_{\text{vap}}$ should be 0.5. It is evident, however, that this ratio must depend on the co-ordination number C_σ in the surface in comparison with C_b for the bulk, so that Stefan's ratio can be written

$$\frac{E_\sigma}{\Delta L_{\text{vap}}} = 1 - \frac{C_\sigma}{C_b} \quad (4)$$

The co-ordination number for the bulk in the case of water has been discussed in a number of publications^{20–25} and is found from the radial distribution function. It is known in the case of water for various temperatures^{20,21}. Data for some other liquids²³, including methanol^{24,25}, argon^{23,26}, Cl_2 , are also known. C_b is sensitive to temperature so some standardized corresponding tem-

perature is desirable²⁷ (e. g. the m. p. or triple point) at which C_b is to be expressed.

Data for S_σ , $S_\sigma/\Delta S_{vap}$ and Stefan's ratio $E_\sigma/\Delta L_{vap}$ calculated from surface tension measurements in the literature, are given in Table I for Hg, Ar, CCl_4 (close-packed, unstructured liquids) in comparison with water and methanol (H-bonded, structured liquids).

TABLE I
Relations Between Surface and Bulk Properties for Some Liquids*

Liquid	S_σ (J. K ⁻¹ mol ⁻¹)	$S_\sigma/\Delta S_{vap}$	S_σ/S_{liq}	$E_\sigma/\Delta L_{vap}$ (Stefan's Ratio)	C_σ/C_b
Mercury	3.60	0.042	0.047	0.44	0.56
Argon	18.7	0.26	0.415	0.42	0.58
Carbon tetra- chloride	15.7	0.185	0.212	0.30	0.70
Methanol	9.0	0.080	0.072	0.13	0.87
Water	8.42	0.079	0.121	0.085 (0 °C) 0.083 (90 °C)	0.915 0.917

* Based on surface tension and density data from International Critical Tables and from refs. 23, 26 and 27.

The interesting result is found that Stefan's ratio is not really 0.5 but less, indicating that the state of molecules in the surface of a liquid is nearer to that in the bulk than would be the case if $E_\sigma/\Delta L_{vap}$ were 0.5, i. e. $C_\sigma/C_b > 0.5$.

This deviation from 0.5 is especially large for the H-bonded liquids H_2O and CH_3OH (Table I) where C_σ/C_b is seen to be ca. 0.87 to 0.9. Thus, such liquids attempt to retain the co-ordination they have in bulk due to the large energy advantage associated with maintaining maximum H-bonding in the interface. Correspondingly, the superficial excess entropy, S_σ , is low for H_2O and CH_3OH compared with Ar and CCl_4 and S_σ is a small fraction of ΔS_{vap} (column 3, Table I). S_σ is also low for Hg presumably due to the metallic bonding in that liquid.

It will be expected that S_σ or $S_\sigma/\Delta S_{vap}$ are related to the internal cohesive forces in the liquid, e. g. as measured by the cohesive energy density (c. e. d.) defined as the ratio $\Delta L_{vap}/[\text{molar}] \text{volume}$, i. e. $\Delta L_{vap} \rho/M$. Figure 1 shows the dependence of S_σ on c. e. d. and it is seen that liquids with high c. e. d. tend to have low S_σ values.

It is to be concluded from the values of $S_\sigma/\Delta S_{vap}$ and $E_\sigma/\Delta L_{vap}$ that the surfaces of water and methanol exhibit an unusually large degree of structure in comparison with close-packed liquids so that this factor will be important in ion solvation at the interface in addition to the electrostatic factors, especially for low charge-density ions which are less repelled from the structured interfacial region and thus can interact with it more specifically.

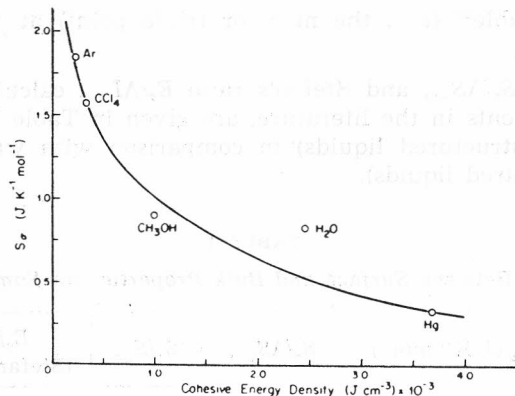


Figure 1. Dependence of S_e on cohesive energy density of a series of 5 liquids.

(ii) Co-ordination and Surface Structure

The values of Stefan's ratio for H_2O and CH_3OH imply that molecules in the surface are far from a »half-way state« between the bulk and the vapor. The significance of values of Stefan's ratio which were expected to be 0.5, and are indeed near 0.5 for unstructured liquids, must, however, be looked at in the light of the surface of crystalline solids when liquids such as H_2O are considered. The Kossel-Stranski, Cabrera-Frank models of crystal growth identify the kink site in an edge of the crystal surface as the critical representative repeating site. This type of site is important because it has *half* the co-ordination number of the bulk, yet the *same* energy. Thus, a particle can be imagined to be transferred from the bulk to the vapor phase by creating a hole in the lattice with energy c. n. $\times U_{11}$ and redeposited at a kink site with an energy $-\frac{1}{2}$ c. n. $\times U_{11}$. Also, the hole in the bulk is closed up with release of energy $-\frac{1}{2}$ c. n. $\times U_{11}$, so the overall energy change for transferring a particle from bulk to a kink site on the surface is zero; in the above, c. n. is the bulk co-ordination number and U_{11} the pairwise interaction energy between particles in the crystal.

In order to account for $E_s/\Delta L_{\text{vap}}$ values as low as 0.08 (Table I), it would have to be supposed that the energy of particles in the liquid surface corresponds more to co-ordination at »kink-like« sites where local energies are close to the bulk energy, than to co-ordination in a flat plane. Bent H-bonds would be involved. The critical significance of kink-type sites is that a particle can be removed (or deposited) *without* creation of a hole or vacancy while transfer of a particle from bulk to a *flat* element of surface would require creation of a surface hole by breaking five $\frac{1}{4}$ — bonds in the (100) type plane or nine $\frac{1}{2}$ — bonds in the (111) close-packed plane (hexagonal lattice). The relative co-ordination numbers in such surfaces would be $\frac{5}{6}$ for a cubic lattice and $\frac{9}{12}$ for the hexagonal one.

(iii) Ionic Adsorption and Solvent-structure Effects Near Interfaces

Most real liquids, especially water, have an interface in which some net degree of solvent orientation arises corresponding to minimization of surface

free energy. In the case of water, the H atoms of H_2O molecules in the surface are oriented inwards towards the bulk²⁸. For hydrated ions near the interface, this will introduce some ion-specific »co-sphere« interaction effect⁵⁸ (analogous to that between ions themselves in the bulk at appreciable concentrations). The effect will arise because the structure-changed region near the ion^{29,30} will overlap with any structure-changed region at or near the surface of the liquid itself (Figure 2) and lead to an additional positive or

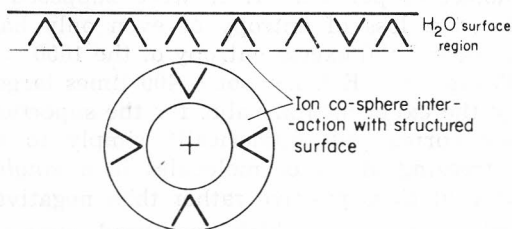


Figure 2. Schematic representation of juxtaposition of oriented water at an interface with water molecules oriented in the hydration shell of an ion.

negative contribution to the free energy of adsorption leading to local diminution or increase of the ionic concentration near the interface. By comparison with hydration co-sphere structure-interactions between ions in the bulk of water solutions, or in the double-layer³¹, it may be anticipated that this effect could amount to at least $\pm 4-6$ kJ mol.⁻¹, due to H-bond breaking or reorientation effects.

The possibility that short-range structure effects at water interfaces are significant in the adsorption of ions is indicated by the unexpected results of Jones and Ray³² that for low concentrations of electrolytes (KCl, CsNO₃ and K₂SO₄) there is initially a decrease of surface tension, i.e. in the opposite sense to the predictions of electrostatic theories,^{8,9} followed by an increase above 0.001 ~ 0.002 molar, (the generally accepted behavior). However, these effects are experimentally controversial.^{33,34}

In cases where an ion is »hydrophobic«, e.g. organic ions with large alkyl chains, positive adsorption will usually arise due to the competition between the tendency for the hydrophobic hydrocarbon residue to be »squeezed out« from the bulk water and the ionic charge to be repelled from the interface where its hydration is restricted. Usually significant positive adsorption arises, e.g. with carboxylate ions and aminium ions, when the number of CH₂-groups in the alkyl chain exceeds 3 or 4. For longer chains salts, e.g. >C₉, C₁₀, micelle formation occurs and the salts are extremely surface active with large positive adsorption.

Over a number of years, there has accumulated controversial evidence that there is a thick structured region, 100-1000 Å in depth, near the interfaces of liquids, especially water. Henniker³⁵ gave a thorough review of the situation as seen in 1949 and the question has been more recently discussed by Drost-Hansen³⁶. The evidence that a structured ice-like layer of water exists near interfaces of aqueous media has, however, become weakened by the indication, now found by a number of workers, that Deryjagin's »polywater«, supposedly formed in quartz capillaries, was an artefact. Correspondingly, the thermodynamics of adsorption at water interfaces and of the interphase itself, are

inconsistent with the water having special properties in a layer more than 1—2 molecules in thickness. From the superficial excess entropy S_σ alone, which has a mean value for the air/water interface of $0.155 \text{ erg. cm}^{-2} \text{ K}^{-1}$ (over 0—50 °C range) or *ca.* $8.42 \text{ J. mol}^{-1} \text{ K}^{-1}$ (see below), it can be seen from the following argument that this value cannot be consistent with any appreciable depth of orientation and structure of water near the interface. For the supposed layer 1000 Å in thickness³⁵, there would exist approximately 300×10^{15} water molecules per cm^2 . If it were supposed that these water molecules had suffered a loss of entropy of even only half the entropy of freezing (-6 e. u.) the superficial excess entropy of the 1000 Å thick interphasial layer would be $-63 \text{ erg. cm}^{-2} \text{ K}^{-1}$, *i. e.* some 400 times larger than the observed value. Evidently the experimental value for the superficial excess entropy of the water surface corresponds numerically simply to about 30% of the entropy change on freezing of water molecules in a *single* layer. However, in any case, the value of S_σ is positive rather than negative.

A second general objection to a thick structured layer at water interfaces is the magnitude of the force field that would be required to maintain an ordered, oriented structure over such a distance. Orientation can only be maintained against the thermal fluctuations in the fluid if the energy associated with the orientation is large compared with kT (Boltzmann's Law) and, so long as the phase remains fluid, a very long-range force field would be required to establish such a situation. Even with the intense coulombic field of ions, $ze/\epsilon r^2$, orientation effects are attenuated to negligible magnitude within 2 water molecules distance from an ion.

In the case of water at a metal interface, effective continuation of the dipole (hydrogen-bond) interactions among the water molecules »through« the interface can occur on account of the dipole images and their interactions with the parent charge distributions on the solution side. Hence a metal surface (unless it is charged) will not be so »structure-breaking« as a non-metallic surface.

Hydrophobic Effects in Ion and Molecule Adsorption

(i) General Factors

Most non-polar solutes have a positive standard free energy of solution in water^{3,37}; this arises for two reasons: (a) the presence of the solute requires a cavity in the solvent⁴ which involves changes in the H-bond equilibrium of the water, with some H-bond breaking, at the boundary of the cavity. This is associated with a positive ΔH^0 term which is usually not completely compensated by the negative ΔH^0 associated with solute-solvent van der Waals interaction; (b) in water as solvent, there is also usually a relatively large negative ΔS^0 term associated with water structure-promotion caused by the non-polar solute.

As a consequence of the positive ΔG^0 of solution, non-polar solutes tend to be expelled from the bulk to any interface. At solid interfaces, they can lose further energy by interaction with the material of the interface as at Hg and other electrodes, or at the air/water interface they can reside wholly or partially »on« the liquid surface as in the case of spreading oils or the hydrocarbon tails of detergent molecules. In the case of a hydrophobic surface

such as that of Teflon or some sulphide minerals, a hydrophobic solute will be positively adsorbed on account of the hydrophobic interaction effect of the type discussed by Kauzmann² and by Ben-Naim³ when both interfaces (*i. e.* of the solid and the solute) tend to minimize their unfavourable interaction with water.

A statistical-mechanical treatment of hydrophobic interaction effects was given by Ben-Naim for simple non-polar molecules on the basis of free energies of solution of »monomer« and equivalent »dimer« species, associated on account of »hydrophobic bonding«. The case of CH₄ and C₂H₆ (»dimer of methane«) was considered; the free energy of hydrophobic association was expressed as the difference of the standard free energies of solution, $\Delta\mu^0$ C₂H₆ - 2 $\Delta\mu^0$, of ethane and methane.

Despite the elegant statistical-mechanical presentation of the hydrophobic interaction effect by Ben-Naim, its evaluation is referred to the difference of relatively simple empirical quantities such as $\Delta\mu^0$ C₂H₆ and $\Delta\mu^0$ CH₄, the standard free energies of solution of 2 CH₄ and C₂H₆. An equally interesting approach can be made in terms of surface tension and cavity area.

The energy of forming a cavity in a fluid can be related to the energy required for generation of its surface, through the surface tension³⁸. This approach has been employed successfully in the free-volume treatment of liquids^{38,39}, despite the fact that mean cavity sizes are comparable with dimensions of individual molecules. Also, Miller and Hildebrand⁴⁰ attributed the observed relation of entropies of solution to the 2/3 power of solute volume, to the entropy of the cavity boundary.

If two particles of radius r and co-sphere hydration radius r_h coalesce with sharing of hydration shells, as in Figure 3, the difference of exposed co-sphere area (the cavity area) is given⁴ by

$$\Delta A = 8\pi r_h^2 [1 - 1/2 (1 + r/r_h)] \tag{5}$$

and the corresponding surface free energy change is $\gamma (\Delta A)$. When $r_h = r$, no advantage in coalescence arises (Figure 3a), of course.

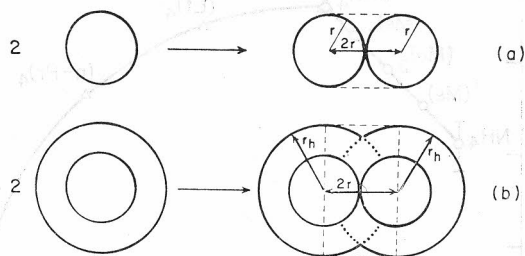


Figure 3. Sharing of hydration co-spheres in hydrophobic association of two particles of radii r and co-sphere radii r_h .

However, taking $r = 1.4 \text{ \AA}$ and $r_h = 2.8 \text{ \AA}$, say, for CH₄ in water and the surface tension γ of water at 25 °C, as 72 erg. cm⁻², we find the energy advantage of co-sphere sharing is $-1/48\pi r_h^2 \gamma$ erg. particle⁻¹. This is equivalent to an energy of

$$\frac{-2\pi (2.8)^2 \times 10^{-10} \times 72 \times 6 \times 10^{23}}{4.18 \times 10^{10}} \text{ kcal (mole pair)}^{-1}$$

or $-2.55 \text{ kcal mole}^{-1}$. This is in quite good agreement with the estimate ($-2.2 \text{ kcal mole}^{-1}$) of hydrophobic interaction of methane given by Ben-Naim³ (his Figure 8). A lower figure would obviously arise if r_h were taken less than $r_{\text{CH}_4} + r_{\text{H}_2\text{O}}$ — probably a maximum figure, since the effective »surface-tension« surface of the cavity probably lies nearer to the solute than the locus of centres of water molecules.

For alcohols, the lyophobic interaction is less³, e.g. by a factor of ca. 1.8 for methanol. The ratio of surface tension of water to that of methanol is 2.9. The effect is in the correct direction but for reasons connected with the different geometries of H_2O and CH_3OH , the ratio r/r_h will not be the same. However, the temperature dependence of the effect is complex and difficult to account for.

Following the relation between hydrophobic interaction effects and standard free energies of solution³, it may be expected that the standard free energies of adsorption at the air/water interface are proportional to the standard free energies of solution and would be at least half the numerical value of the latter quantity. This type of relation is borne out by the proportionality of adsorbability (free energy of adsorption) to number of $-\text{CH}_2-$ groups in paraffinic hydrocarbon residues in non-polar surfactants and the similar relation between solubility and chain length.

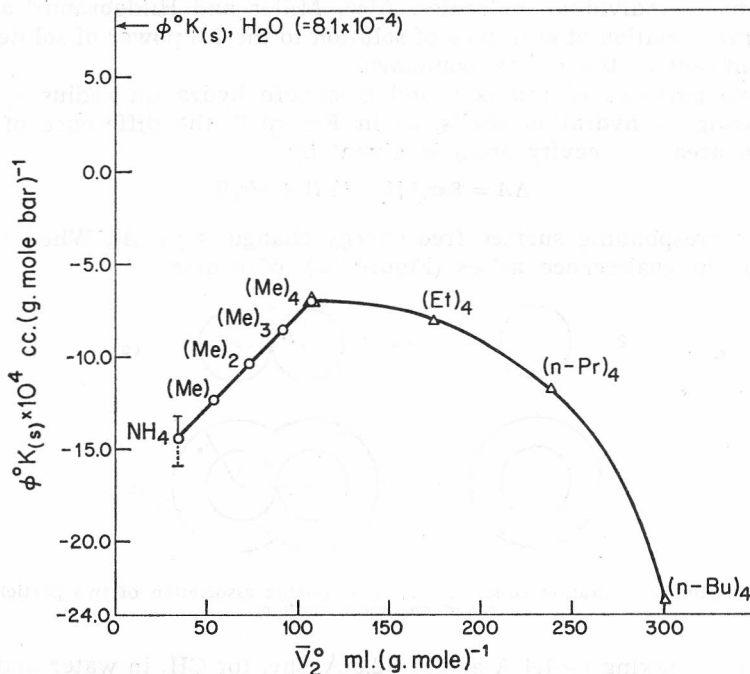


Figure 4. Transition from hydrophilic to hydrophobic ion-solvent interaction in a series of methylammonium and tetra-alkylammonium salts (from ref. 42).

* Based on work of R. Bennes and B. E. Conway to be published more fully elsewhere.

(ii) Adsorption of Alkylammonium Ions at the Air/Water Interface*

Ions of the type $R_nNH_{4-n}^+$ present an interesting series in which hydrophobicity and electrostatic ion-solvent interaction can be varied systematically. The solution properties (partial molar volume and compressibility) of a series of ions of this type were studied by Conway and Verrall⁴¹ and by Mathieson and Conway⁴² who demonstrated a clear transition from hydrophilic to hydrophobic behavior as n was increased from zero to 4 with $R = \text{Me}$, and with $n = 4$ as R was changed successively in an homologous series from Me to $n\text{-Bu}$ (Figure 4).

Bennes and Conway* measured the adsorption of a series of organic ions of the above type (as perchlorates) with $R = n\text{-propyl}$ at the air/water interface by the du Nouy ring method and simultaneously obtained the changes of surface potential, $\Delta\chi$, by the Kelvin method.

$\Delta\chi$ is displaced to more positive values as the concentration of $(n\text{-Pr})_nNH_{4-n}^+$ ion is increased but the displacement is less in the order $\text{Pr}NH_3^+ > \text{Pr}_2NH_2^+ > \text{Pr}_3NH^+ > \text{Pr}_4N$. The relative effects are easily demonstrated by plotting $\Delta\chi$ vs $\log c$ and evaluating the slopes which are analogous to Esin and Markov coefficients in electrochemical studies of adsorption at the Hg electrode. Figure 5 shows such plots while Table II shows how the

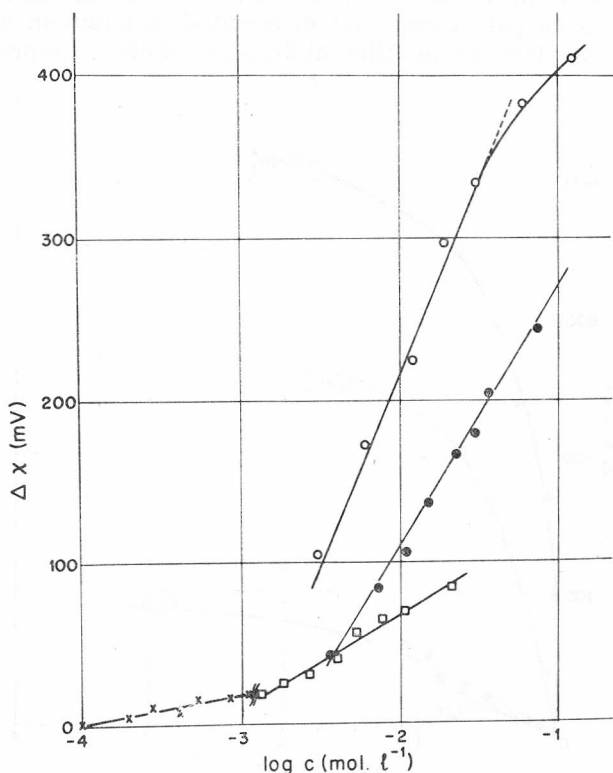


Figure 5. Dependence of $\Delta\chi$ for the air/water interface on \log [concentration] of various n -propylamine perchlorates and $(n\text{-Pr})_4NClO_4$ (25 °C): \times Pr_4N^+ ; \square Pr_3NH^+ ; \bullet $\text{Pr}_2NH_2^+$; \circ PrNH_3^+ .

slopes $d\Delta\chi/d \log c$ depend on the number of n -Pr chains or total number of C atoms (as CH_2 or CH_3).

TABLE II

Salt Cation	$d\Delta\chi/2.3 \log c$
$n\text{-PrNH}_3^+$	$3.97(\text{RT}/F)$
$(n\text{-Pr})_2\text{NH}_2^+$	$2.66(\text{RT}/F)$
$(n\text{-Pr})_3\text{NH}^+$	$1.0(\text{RT}/F)$
$(n\text{-Pr})_4\text{N}^+$	$0.3(\text{RT}/F)$

The significance of $\Delta\chi$ values is usually more easy to interpret if $\Delta\chi$ is plotted, as in Figure 6, *vs.* the surface excess Γ measured in the adsorption experiment. While $n\text{-Pr}_4\text{N}^+\text{ClO}_4^-$ is the most strongly adsorbed salt, it is evident from Figure 6 that it produces the *smallest* relative change of surface potential. In fact, Figure 6 shows that the changes of surface potential *decrease* with increasing hydrophobicity while the adsorbability, as measured by Γ values, increases in this direction, as expected.

The changes of surface potential caused by salts at the air/water interface arise for three principal reasons: (a) differential distribution of cations and anions near the interface due to different distances of closest approach connected

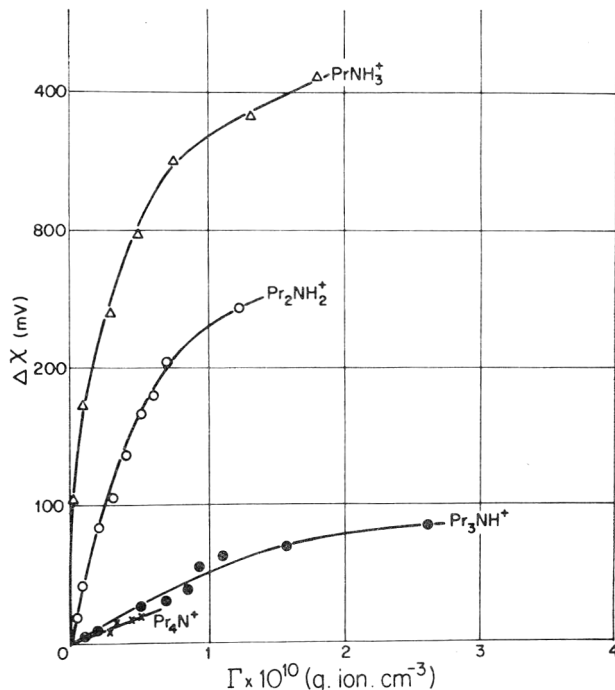


Figure 6. $\Delta\chi$ values of Figure 5 plotted against the surface excess, Γ , of the adsorbed propylamine ions.

with different radii of primary solvation shells (Figure 2) of cations and anions. This gives rise to a double-layer p. d. near the interface; (b) differential distribution of cations and anions near the interface due to different charges on the ions¹⁰ (inapplicable to the present experiments); (c) effects of the ion on the intrinsic surface dipole p. d. at the water interface arising from residual net orientation of H₂O dipoles; and (d), connected with (c) above, any interaction of the hydration co-sphere of the ion with oriented water dipoles at the surface, (Figure 2). Factors (a) and (c) will probably be the most important ones in the adsorption behavior of the alkylammonium ions.

The values of $\Delta\chi$ for $n\text{-PrNH}_3^+$ and $(n\text{-Pr})_2\text{NH}_2^+$ are relatively large in comparison with those generated by simple salts. Large values, but at higher concentrations were also found by Frumkin⁴³, Randles⁴⁴ and by Zagorska and Koczorowski⁴⁵ in the case of Me_4N^+ and Et_4N^+ salts. However, these $\Delta\chi$ values are opposite in sign from those for simple salts and for the present alkylamine salts.

The results show that the ions which are most strongly (positively) adsorbed give the least change of surface potential. This trend is closely connected with the extent of hydration of the alkylammonium cations as measured, e. g. by the electrostriction or the partial molal adiabatic compressibility^{41,42}. Thus, Figure 7 shows how $d\Delta\chi/2.3 d \log c$ for the $n\text{-Pr}$ series of salts varies with the partial molal compressibility and electrostriction (relative to $n\text{-Pr}_4\text{N}^+$) of a corresponding series of methyl-ammonium or $n\text{-propyl}$ -ammonium salts. It is clear from these plots that the stronger the cation-water interaction, the less is the cation adsorbed but the greater is the relative change of surface potential.

This trend of the data in Figure 7 may be rationalized by noting (a) that the more strongly an ion is hydrated, the greater is the tendency for it to be repelled from the surface in order to minimize restriction of its interaction with the solvent dielectric; and (b) that the more hydrophobic is the ion (n

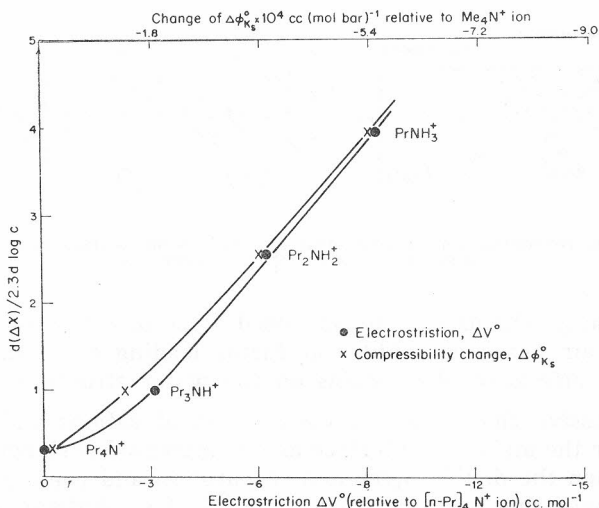


Figure 7. Relation between slopes $d\Delta\chi/d\ln c$ and partial molal compressibility and electrostriction of $\text{R}_n\text{H}_{4-n}\text{N}^+$ salts.

increasing from 0 \rightarrow 4) the greater will be the tendency for it to be displaced out of the bulk water medium into the surface layer region where energetically unfavorable hydrocarbon-water interactions are minimized. Thus, two opposing effects generate the trend of adsorption and surface potential behavior shown in Figures 5—7.

The hydrophobic effect diminishes, as expected, in the case of R_4N^+ salts when the adsorption and $\Delta\chi$ measurements are made in progressively more methanolic solutions in CH_3OH-H_2O mixtures⁴⁵. This is consistent with the observed⁴⁶ lack of »hydro«-phobic interaction behavior of R_4N^+ salts in methanol.

In the behavior of this series of salts, the positive values of Γ do not uniquely signify that the alkylchain resides above the surface in the air phase or the hydrophilic N^+ group just below the surface in the water phase that would otherwise be depleted in the case of simple ions. The measured surface excess is one of cations and anions. Normally a large anion will be distributed up to a plane of closest approach to the interface which is nearer to the interface than that for cations. As the number of chains is increased on the N^+ center, the cation tends to be adsorbed progressively nearer to the surface of separation of the phases so that the difference of position of the planes of approach of added alkylammonium cations and the solution anions tends to be reduced as indicated schematically in Figure 8. The surface potential contribution due to the ionic double-layer then tends to become diminished.

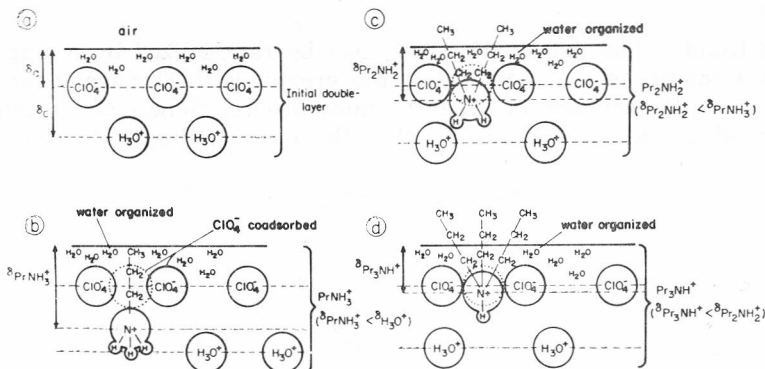


Figure 8. Schematic representation of distribution of cations and anions near the water surface in solutions of $(n-Pr)_nN^+H_{4-n}$ perchlorates.

Since the alkyl chains may be supposed to be directed towards, or reside partly in, the air phase an additional factor leading to a change of χ will arise from the effects of alkyl chains on the water structure at the surface.

The progressive change of the distribution of cations and anions in the interphase near the air/water interface as n is increased is shown schematically in Figure 8 when the double-layer ionic separation and consequent p. d. diminishes with increasing positive adsorption of the alkylammonium ion. An analogous situation arises at the Hg/water interface as envisaged by Hayter and Hunter⁴⁷ for $R_3R'N^+$ ions.

Electrostatic Effects in Ion Adsorption at a Liquid Interface

(i) *Electrostatic polarization energy*

When an ion is transferred from the bulk solvent medium to a position near the interface of the solvent, it experiences a change of electrostatic polarization energy. This may be calculated by means of the Born equation for various model situations of the ion.⁵⁸

The polarization effects in ion adsorption are considered at infinite dilution to eliminate ionic atmosphere effects^{9,10} which screen the ion/ion-image repulsion^{8,9} at finite concentrations.

Case (a): *Born model for total hydration energy*

The simplest case is that where the ionic solvation is treated according to Born's model⁴⁸. This gives only a preliminary basis for discussing the problem, since it is well known that the Born equation cannot be expected to apply at short distances from the ion itself without corrections for dielectric saturation or introduction of a change of model in this region.

Consider, first, the Born energy of an ion in the solution and in the surface (Figure 9a). The charging energy for the ion of radius r_i in solution is

$$G_s = \frac{(ze)^2}{2\epsilon r_i} \tag{6}$$

For the model of an ion in the surface, we may imagine that half the charge is brought up in vacuo and half in solution, giving the charging energy, G_σ , in the surface. A positive energy of adsorption due to hydration energy change then arises and is given by

$$\Delta G_{ads} = G_\sigma - G_s = \frac{(ze)^2}{2 r_i} \left(1 + \frac{1}{\epsilon} \right) - \frac{ze^2}{2 r_i} \left(\frac{1}{\epsilon} \right) = \frac{(ze)^2}{4 r_i} \left(1 - \frac{1}{\epsilon} \right) \tag{7}$$

which is half of the desolvation energy of the ion, as expected from Figure 9a. It is obvious that the model in Figure 9a corresponds only to an extreme case. A distribution of positions of the ion will be taken up (see below) corresponding to a range of hydration energies near the surface, on the solution-side of the interface. Also, the primary hydration shell of the ion must be considered.

Case (b): *Ion below liquid interface*

The more general case is that where the ion is centered at some position, l , below the liquid interface (Figure 9b). The hydration energy of the ion can be treated in terms of the ion's self-energy in the bulk dielectric medium diminished by the energy that would have been associated with the region of bulk solvent unavailable to the ion beyond the nearby surface of liquid, but to which is added the charging energy associated with the same volume in the free space above the liquid where $\epsilon' = 1$ (Figure 10).

A model (Figure 9b) is considered where the ion is at a distance l from the surface. Spherical volume elements above the liquid are centered on the ion, but at distances x from the surface (Figure 10). The polarization energy due to the ionic field E is calculated below and above the dividing surface, where the dielectric constants are ϵ and $\epsilon' (= 1)$, respectively.

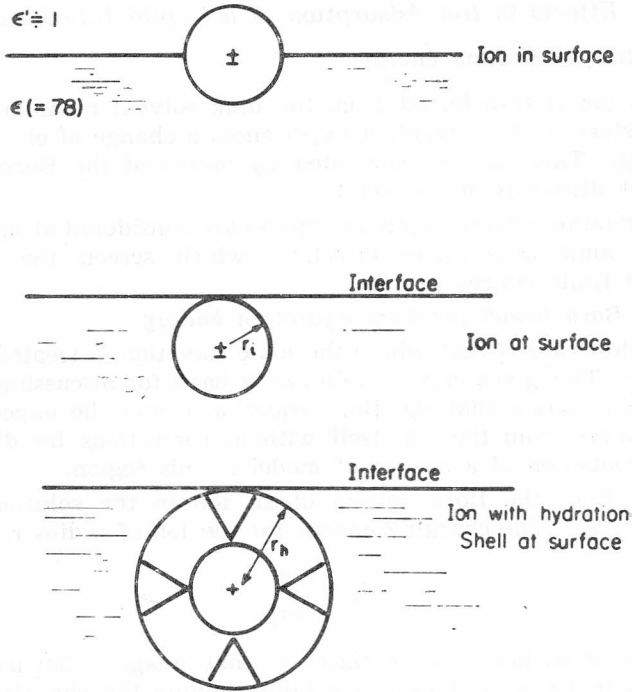


Figure 9. Representations of an ion near a liquid surface
 a) Ion in liquid surface
 b) Ion below liquid surface

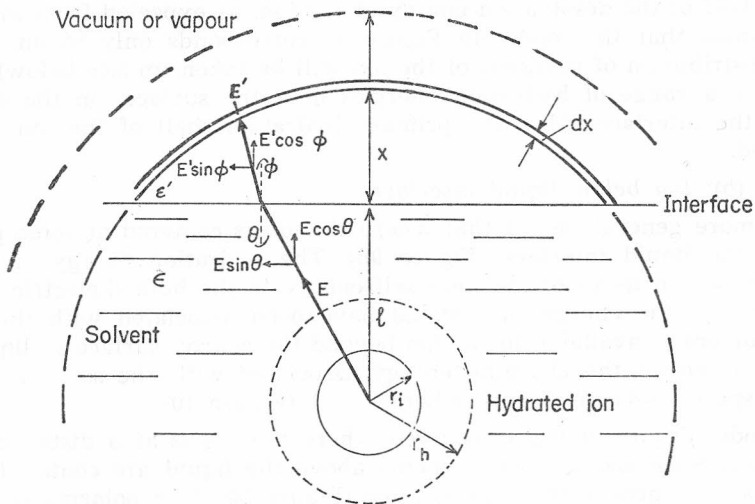


Figure 10. Model for calculation of polarization energy of an ion near to and below a liquid surface.

At the interface of two dielectrics across which a field exists, three conditions apply: (a) the potential has a common value at the interface, (b) the normal components of the dielectric displacements D just within and just outside the interface are equal and (c) the tangential components of the field on each side of the interface are equal. At the dielectric discontinuity, the direction of field vectors also changes from an angle ϑ to an angle φ to the normal to the surface (see Figure 10). These conditions give

$$\epsilon E \cos \vartheta = \epsilon' E' \cos \varphi \text{ and } E \sin \varphi = E' \sin \vartheta \tag{8}$$

The field vector outside the liquid surface, E' , is hence, since $\epsilon' = 1$,

$$E' = E [\epsilon^2 \cos^2 \vartheta + \sin^2 \vartheta]^{1/2} \tag{9}$$

or since $\epsilon^2 \gg 1$ for water,

$$E' \doteq E \epsilon \cos \vartheta$$

The work of charging the ion is $\epsilon \int (E^2/8\pi) dV$, where E is the ionic field and dV is the volume element in which polarization due to the ionic field arises. For the volume above the surface, the charging energy contribution, if it were still for the fluid of dielectric constant ϵ , is seen from Figure 10 to be

$$G = \frac{\epsilon e^2}{8\pi} \int_0^\infty \frac{2\pi(l+x)x dx}{\epsilon^2(l+x)^4} = \frac{\epsilon e^2}{8\pi} \int_0^\infty \frac{x dx}{\epsilon^2(l+x)^3} \tag{10}$$

since the area of the spherical sector (Figure 10) is $2\pi(l+x)x$ and its volume is $2\pi(l+x)x dx$. Then

$$G = \frac{e^2}{4\epsilon} \left[-\frac{1}{l+x} + \frac{1}{2(l+x)^2} \right]_0^\infty = \frac{e^2}{81\epsilon} \tag{11}$$

for an ion of charge e and $\epsilon (= \epsilon')$ is to be taken as 1 above the interface.

The calculation of the remaining polarization energy due to E' in the spherical shells dx in the free space above the interface presents substantial mathematical difficulties since it involves integration over x and various solid angles determined by $\varphi = \arctan [\epsilon'/\epsilon \tan \vartheta]$. If, however, the main polarization effect of the ion were attributed to a spherical angle for which $\cos \vartheta$ is near 1 (which is equivalent to neglecting the refraction of lines of force), $E' = \epsilon E$, so that for an ion of radius r_i at the position $l = r_i$, $G_\sigma \doteq e^2/8r_i$ above the surface and its self-energy in the bulk is $e^2/2\epsilon r_i$. If the bulk extended above the dividing interface, the charging energy contribution in the medium above the surface would be $e^2/8\epsilon r_i$ from eqn. 11. Hence, the net charging energy for the ion in the situation shown in Figure 9b would be very approximately*

$$G_\sigma = \left[\frac{e^2}{2\epsilon r_i} - \frac{e^2}{8\epsilon r_i} + \frac{e^2}{8r_i} \right] = \frac{e^2}{8r_i} \left(\frac{3}{\epsilon} + 1 \right) \tag{12}$$

* It is interesting that the terms $\frac{e^2}{2\epsilon r_i} - \frac{e^2}{8\epsilon r_i} \left(= \frac{3}{8} \frac{e^2}{\epsilon r_i} \right)$ in eqn. (12), which arise from eqns. (6) and (10) without any approximations, and correspond to the charging energy with respect to the solvent fluid available to the ion below the dividing surface, give G_σ already larger than does the image energy calculation [8, 9].

The self-energy in the bulk, as mentioned above, is $(e^2/2\epsilon r_i)$, so the energy of adsorption of the ion in the situation shown in Figure 9b will be approximately

$$\Delta G_{\text{ads}} = G_c - G_s = \frac{e^2}{8r_i} \left(\frac{3}{\epsilon} + 1 \right) - \frac{e^2}{2\epsilon r_i} = \frac{e^2}{8r_i} \left(1 - \frac{1}{\epsilon} \right) \quad (13)$$

a quantity which is always positive, corresponding to negative adsorption.

Case (c): *Ion with primary hydration shell near the interface.*

Equation (8) would predict a large positive ΔG_{ads} if r_i were taken as the crystal ionic radius. However, it is much more probable (cf.²⁸) that ions in the surface region of the liquid interface do *not* lose their primary hydration layer⁴⁹ because this is a region of high ion-solvent interaction energy. Hence, because of the strong interaction within the primary hydration shell of radius r_h , almost no ions will be able to approach the liquid surface to distances $l < r_h$. The restriction on extent of hydration which ions near a liquid surface must suffer hence arises principally from loss of long-range Born polarization energy *beyond* r_h .

The model (Figure 2) in which a fixed primary hydration shell is assumed allows a Born treatment to be pursued more reliably since it is applied only to the solvent polarization beyond (cf.^{29,50}) the primary hydration shell where ϵ can be taken as the bulk value and the molecular structure of the solvent is then also less important than it is near the ion. However, the structure-broken region (Frank and Evans³⁰) just outside the primary shell will also be important, as discussed earlier.

Pursuing this approach by taking $l = r_h$ for the above case, and using eqn. (13) gives

$$\Delta G_{\text{ads}} = \frac{e^2}{8r_h} (1 - 1/\epsilon) \quad (14)$$

For Na^+ , r_h is approximately $0.95 + 2.76 \text{ \AA}$ which gives $\Delta G_{\text{ads}} = 10 \text{ kcal. mol}^{-1}$. This energy is sufficiently large to more or less completely exclude the ion from the surface region at $l \leq r_h$ at ordinary temperatures (exp. $-10,000/600 \approx 10^{-7.2}$).

(ii) *Distribution of Hydrated Ions near a Liquid/Vapour Interface*

It is evident that a distribution of ions will be generated near the surface according as ΔG_{ads} becomes smaller with increasing l as $l \geq r_h$. The net surface excess must then be calculated by integration of this distribution with respect to l away from the surface. By integrating over a distance $l = r_h$ to ∞ away from the surface, the surface excess is

$$\Gamma_i \doteq c_o \int_{r_h}^{\infty} \left[\exp \left\{ - \frac{Ne^2}{8lRT} (1 - 1/\epsilon) \right\} - 1 \right] dl \quad (15)$$

where N is Avogadro's number and ϵ can be considered almost constant with l for $l \geq r_h$. Equation (15) involves an exponential integral function and must

be evaluated numerically (Figure 11) so that Γ_i can be calculated. It is to be noted that from the electrostatic treatment of energy of hydration of ions near an air/water interface, Γ_i is always negative as found experimentally for simple ions.

Mathematical problems of convergence (cf.,^{8,9}) arise with equation (15) with ∞ as the upper limit of the integral which are avoided at finite concentrations in the image treatment⁹ by introduction of the Debye-Hückel screening distance $1/\kappa$. To obtain a limiting results for $(\Gamma_i/c_0)_{C_0 \rightarrow 0}$ it seems necessary to make an empirical restriction to the upper limit of the integral of eqn. (15), from ∞ to a distance L . It seems reasonable to choose L as the distance at which the Born co-sphere overlap energy with the interface is $\leq kT$. Then, based on eqn. (14), L will be $\frac{e^2}{8kT} (1 - \frac{1}{\epsilon})$ which has a value of 60 Å for a univalent ion in water at 298 K.

Figure 11 shows the course of $-\Gamma_i/c_0$ as a function of the distance of i over which Γ_i is integrated and also the dependence of the distribution function $\exp -K/l$, where $K = \frac{Ne^2}{8RT} (1 - \frac{1}{\epsilon})$, on l , the distance from the interface. At the limit $l = L$ where $\Delta G_{ads} \leq kT$, the surface excess of ions near the interface of a 0.1 M solution of a univalent salt is -5.6×10^{-11} mole cm^{-2} , or $\pm 5.6 \mu\text{c}.\text{cm}^{-2}$ for a given ion type (this is a surface excess comparable to that in the double-layer at Hg at low charge densities.)

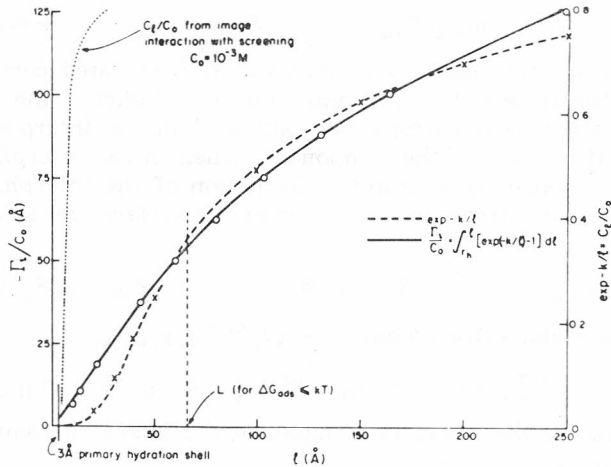


Figure 11. Integration of eqn. (15) giving the distribution of a univalent ion near a water surface in the absence of ionic atmosphere effects. Data of Onsager and Samaras⁹ for a finite concentration are shown for comparison.

Equation (15) gives the Γ_i arising only from restriction of hydration near the surface at infinite dilution. Ionic atmosphere screening effects^{9,10} cause Γ_i/c_0 to be much diminished from the infinite dilution values as shown in Figure 11.

Entropy of Adsorption and Orientation of Water in the Double-Layer at Charged Interfaces

(i) Treatment of Experimental Data

Information on the hydration of charged electrode interfaces can be obtained indirectly from (a) the overall excess entropy I_s of an interphase derived from $I_s = -\left(\frac{\partial\gamma}{\partial T}\right)_{P, n_1, n_2, \dots}$ or (b) from the entropy of adsorption of a substance that displaces previously adsorbed solvent. Method (a) involves contributions to I_s both from the excess entropy of the solvent at the interface and the entropy associated with any adsorption of solute species⁵¹; method (b) involves the difference of entropy of the adsorbate in solution and at the interface, and the entropy of displacement of the solvent from the surface⁵ in an amount corresponding to the effective area requirement of the adsorbate.

Hills and Payne⁵², and Hills and Hsieh⁵³, using method (a), measured the surface excess entropies I_s of the Hg-solution interface for various salt solutions and found I_s was sensitive to the anion present at potentials positive to the potential of zero charge, as expected. Conway and Gordon⁵¹ pointed out that I_s is, however, a complex quantity composed of contributions due to adsorption and orientation of solvent and accumulation of ions in the interphase which are associated with a certain partial molar entropy.

Harrison, Randles and Schiffrin⁵⁴ made a thermodynamic analysis of the question of the entropy of formation of a charged interphase ΔS_{m-soln} , taking into account the above contributions⁵¹, and wrote

$$\Delta S_{m-soln} = S^\sigma - m_{Hg}^\sigma S_{Hg}^\sigma - m_{H_2O}^\sigma \bar{S}_{H_2O} - m_+^\sigma \bar{S}_+ - m_-^\sigma \bar{S}_- \quad (16)$$

where m terms are the numbers of moles of the indicated component in the interphase, S terms are the entropies and bars indicate the partial molar quantities; S^σ is the total entropy per unit area of the interphase. ΔS_{m-soln} is the difference of entropy of the components when in the interphase and when in solution; it is hence the entropy of formation of the interphase. ΔS_{m-soln} is related to the surface excess entropy I_s and the surface excess of components by the relation

$$\Delta S_{m-soln} = I_s - I_- \bar{S}_- - I_+ \bar{S}_+ = I_s - I_+ \bar{S}_{salt} \pm q_m \bar{S}_\pm F \quad (17)$$

where q_m is the metal surface charge, $-(\partial\gamma/\partial E)_{T, P, n_1, n_2, \dots}$,

$$I_s = S^\sigma - m_{Hg}^\sigma S_{Hg}^\sigma - m_{H_2O}^\sigma (\bar{S}_{H_2O} + \bar{S}_{salt} n_{salt}/n_{H_2O}) \quad (18)$$

and n quantities are the numbers of moles of the indicated components in the bulk solution. Also

$$I_\pm = m_\pm^\sigma - m_{H_2O}^\sigma n_\pm/n_{H_2O} \quad (19)$$

Employing method (b), Conway and Gordon⁵¹ and Conway and Dhar⁵, using the rigid adsorbates pyridine and pyrazine at a mercury electrode, measured the quantities of these substances adsorbed as a function of temperature and potential, or surface charge, and derived their isosteric standard entropies of adsorption. By treating the adsorption in terms of displacement of a number of previously adsorbed and oriented water molecules^{55,56}, they

deduced quantitatively the state of water in the double-layer at the mercury electrode in terms of its entropy as a function of charge on the Hg electrode and of coverage by the organic adsorbate. A statistical-mechanical calculation of the entropy of water in the double-layer was made by Conway and Gordon⁵¹ in terms (a) of mixing of »up« and »down« orientational states⁵⁶, and (b) of field dependence of the librational entropy of water molecules in the double-layer.

Solvent dipole orientation can be considered in terms of the model of Watts-Tobin and Mott⁵⁶, in which dipoles are regarded as being in an up (↑) and down (↓) direction with respect to the surface. This gives rise to a molar configurational entropy of mixing S_c of the two orientational states:

$$S_c = -R [\Theta \downarrow \ln \Theta \downarrow + \Theta \uparrow \ln \Theta \uparrow] \tag{20}$$

where the Θ terms are the surface fractions (and hence relative coverages) of dipoles oriented in ↑ or ↓ directions. The orientation of dipoles is determined by their interaction with the electrode field E and by their mutual interactions⁴⁶. The resulting distribution function for interacting dipoles is given by

$$\frac{N \uparrow - N \downarrow}{N_T} = \tanh \left[-\frac{Uz}{kT} \left(\frac{N \uparrow - N \downarrow}{N_T} \right) + \frac{\mu E}{kT} \right] \tag{21}$$

where U is the interaction energy per pair of dipoles in a configuration with coordination number z and $N \uparrow$, $N \downarrow$ are the numbers of dipoles in ↑ and ↓ orientations respectively, and $N_T = N \uparrow + N \downarrow$. In terms of the relative coverages Θ ,

$$(2\Theta \downarrow) - 1 = \tanh \left[-\frac{Uz}{kT} (2\Theta \uparrow - 1) + \frac{\mu E}{kT} \right] \tag{22}$$

The configurational entropy of the layer of molecules with mixed orientations then follows from eqn. 20. $\Theta \uparrow$ and $\Theta \downarrow$ may be related to q through E given by $E \doteq -4\pi q/\epsilon$ where ϵ is the effective dielectric constant for the surface layer. The problem considered is closely related to that involved in the calculation of magnetization in a lattice of magnetic dipoles. Corrections for non-random mixing when lateral interaction effects are significant are relatively small and to a first-order approximation, are of the order $-R \frac{(\Theta \uparrow \Theta \downarrow)^2}{4z} \left(\frac{zU}{kT} \right)^2$ *i. e.*, the non-randomness introduced by interaction contributes, as expected, a negative term in the entropy of mixing, the maximum value of which amounts to only -0.5 eu for $zU/kT = 5$ say, near $q = 0$.

The most important factor in the entropy of the solvent at a charged electrode interface is associated with librative oscillations of the solvent dipoles in the double-layer field, as in hydration of ions.

The partition function for the libration mode is

$$f_L = \frac{8\pi^2 (8\pi^3 I_1 I_2 I_3 k^3 T^3)^{1/2}}{\sigma h^3} \frac{\sinh [U_e/kT]}{U_e/kT} \tag{23}$$

where U_e is the electrostatic field-dipole interaction energy and I 's are the principal moments of inertia of the water dipole. The entropy associated with the librational energy states in the field is then

$$\frac{S_L}{R} = \ln \frac{8\pi^2 (8\pi^3 I_1 I_2 I_3 k^3 T^3)^{1/2}}{\sigma h^3} - \ln U_e/kT + \ln \sinh [U_e/kT] - \frac{U_e}{kT} \coth \left[\frac{U_e}{kT} \right] + 5/2 \quad (24)$$

so that S_L can be evaluated for various values of the inner Helmholtz field $E = 4\pi q/\epsilon$. S_L as a function of q is shown in Figure 12 for one librational mode. The variation of entropy with q is appreciable and larger than that of S_c with q . It is also approximately linear with U_e , thus providing a basis for the observed compensation between energy and entropy terms.

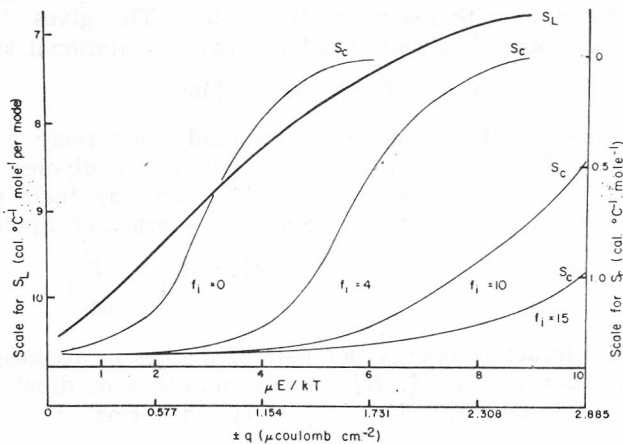


Figure 12. Libration entropy for 1 mode and configurational entropy of water molecules in the double-layer field at a charged interface as a function of $\pm q$; (the curves are symmetrical about $q = 0$).

It can generally be assumed that the internal vibrations of H_2O molecules are little affected by the field at the interface, except indirectly by hydrogen bond bending or breaking effects. In any case, the internal vibrational entropy will be small at room temperatures, since the bend and stretch vibrational quanta are between 8 and 16 kT.

The above treatment provides a basis for interpretation of entropies of substitutional adsorption at the Hg/water interface⁴¹, and gives a reasonable quantitative explanation for the observed entropies of adsorption of pyridine and pyrazine at Hg. In particular, it gives a basis for the increasing positive entropy of adsorption as surface charge, $\pm q$, is increased due to release of low entropy water, previously electrostricted in the double-layer, on account of displacement by the organic adsorbate. This treatment gave a basis for the subsequent conclusion of Hills and Hsieh⁵³ that water at the Hg-aq. interface had maximum entropy at $-4 \mu\text{Coulombs cm}^{-2}$, corresponding to minimum net orientation.

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SAŽETAK

Hidrofobne i elektrostatske interakcije pri adsorpciji na granici faza: Odnos prema prirodi tekućih površina

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Elektrostatske i hidrofobne interakcije iona u blizini granice faza ispitivane su u odnosu na vrstu i strukturu površine tekućina, posebno vode.

Površinski suvišak entropije i energije tekućih površina izračunan je iz podataka o površinskoj napetosti, te je izveden Stefanov omjer za nekoliko tekućih granica faza. Stefanov omjer odnosi se na omjer koordinacijskog broja molekula na površini prema onom u masi otopine i daje informacije o strukturi površine. Stefanov omjer je približno 0,5 za nepolarne tekućine i približno 0,1 za tekućine s H-vezom. Površinski suvišak entropije vezan je za gustoću kohezijske energije i koordinaciju u površini.

Efekti kratkog dometa u adsorpciji iona na granici faza zrak-voda određeni su strukturom tekuće površine i energijom elektrostatske polarizacije u blizini međufaze. Na osnovi Bornove jednadžbe izvedene su relacije za ionsku adsorpciju u blizini tekućih međufaza.

Proučavanjem adsorpcije serije poliamin perklorata na međufazi zrak-voda, te promjene potencijala površine, istražena je relativna važnost hidrofobnih i elektrostatskih interakcija ion-otopalo.

Diskutirane su metode istraživanja adsorpcije vode na nabijenim međufazama i prikazana teorija entropije vode u dvosloju.

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