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1. The Interface Between Aqueous Electrolyte Solutions and the Gas Phase

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Our knowledge of the electrolyte solution–gas phase interface derives principally from two sources; surface-tension measurements and surface-potential measurements. Practically all the existing data refer to aqueous solutions. Some measurements of the surface tension of non-aqueous solutions of inorganic salts have been made (e.g., references 9 and 25), but because of the lack of sufficient additional thermodynamic data for the solutions, calculation of surface excesses is usually impossible. The scope of this article is therefore restricted to aqueous solutions. Surface-tension measurements provide the bulk of the information and

since surface compositions must be derived from these by thermo-dynamic methods, we begin with a brief summary of the relevant thermodynamics.

I. Thermodynamics of a Liquid–Gas Interface

1. Thermodynamics

The total differential of the energy U of a phase is given by

$$dU = T\,dS - P\,dV + \sum_i \mu_i\,dn_i$$

where T, P, S, and V are the temperature, pressure, entropy, and volume of the phase and n_i is the number of moles of component i,
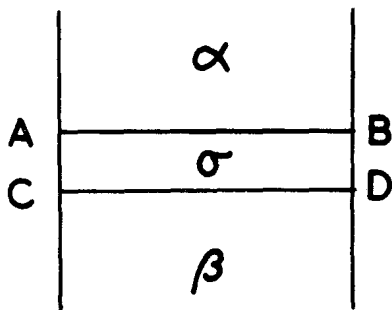
Fig. 1.

whose chemical potential in the phase is μ_i. The corresponding equation for a plane interphase (region σ in Fig. 1) is (15, section 1.53).

$$dU^\sigma = T\,dS^\sigma - P\,dV^\sigma + \gamma\,dA + \sum_i \mu_i\,dn_i \tag{1}$$

where γ is the interfacial tension and A the area of the interface. The terms $\gamma\,dA - P\,dV^\sigma$ represent the work done *on* region σ in increasing its area by dA and its volume by dV^σ, and these replace $-P\,dV$ for a bulk phase. The Gibbs free energy of the interphase is defined by

$$G^\sigma = U^\sigma - TS^\sigma + PV^\sigma - \gamma A \tag{2}$$

from which, with (1)

$$dG^\sigma = -S^\sigma\,dT + V^\sigma\,dP - A\,d\gamma + \sum_i \mu_i\,dn_i \tag{3}$$

whence

$$G^\sigma = \sum_i \mu_i n_i \qquad (4)$$

By differentiating (4) and subtracting (3) we obtain the analog of the Gibbs-Duhem equation

$$S^\sigma \, dT - V^\sigma \, dP + A \, d\gamma + \sum_i n_i^\sigma \, d\mu_i = 0 \qquad (5)$$

We shall be concerned primarily with two-component systems (single solute + solvent), for which

$$S^\sigma \, dT - V^\sigma \, dP + A \, d\gamma + n_1^\sigma \, d\mu_1 + n_2^\sigma \, d\mu_2 = 0 \qquad (6)$$

Since chemical potentials are uniform throughout the system, $d\mu_1$ and $d\mu_2$ may be obtained from the expressions for the bulk liquid phase

$$d\mu_1 = -S_1 \, dT + V_1 \, dP + (\partial\mu_1/\partial x_2)_{T,P} \, dx_2 \qquad (7)$$

and

$$d\mu_2 = -S_2 \, dT + V_2 \, dP + (\partial\mu_2/\partial x_2)_{T,P} \, dx_2 \qquad (8)$$

where S_1, S_2, V_1, and V_2 are partial molal quantities and x_2 is the mole fraction of solute, in the liquid phase. Substituting (7) and (8) in (6)

$$A \, d\gamma + (S^\sigma - n_1^\sigma S_1 - n_2^\sigma S_2) \, dT - (V^\sigma - n_1^\sigma V_1 - n_2^\sigma V_2) \, dP$$
$$+ [n_1^\sigma(\partial\mu_1/\partial x_2) + n_2^\sigma(\partial\mu_2/\partial x_2)] \, dx_2 = 0 \quad (9)$$

The Gibbs-Duhem equation for the liquid phase,

$$n_1\left(\frac{\partial\mu_1}{\partial x_2}\right)_{T,P} + n_2\left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,P} = 0$$

may be used to eliminate either $\partial\mu_1/\partial x_2$ or $\partial\mu_2/\partial x_2$ from (9). If we eliminate $\partial\mu_1/\partial x_2$ and divide through by A we obtain

$$d\gamma + (S^\sigma/A - \Gamma_1 S_1 - \Gamma_2 S_2) \, dT - (V^\sigma/A - \Gamma_1 V_1 - \Gamma_2 V_2) \, dP$$
$$+ [\Gamma_2 - (n_2/n_1)\Gamma_1](\partial\mu_2/\partial x_2) \, dx_2 = 0 \quad (10)$$

where $\Gamma_1 = n_1/A$ and $\Gamma_2 = n_2/A$. In a strictly two-component system dP cannot be zero if T or x_2 is varied because it is the vapor pressure of the solution. However, since the density of the region σ is similar to that of the liquid, the term $(V^\sigma/A - \Gamma_1 V_1 - \Gamma_2 V_2) \, dP$ is negligible, as usual for liquid systems. Also, in practice, the presence of air or other inert gas does not appreciably affect

aqueous surface tensions, and P may in fact be kept constant. Thus, neglecting the term in dP

$$(\partial\gamma/\partial T)_{x_2} = (S^\sigma/A - \Gamma_1 S_1 - \Gamma_2 S_2) = s \qquad (11)$$

$$(\partial\gamma/\partial\mu_2)_T = [\Gamma_2 - (n_2/n_1)\Gamma_1] = \Gamma_{2(1)} \qquad (12)$$

$$(\partial\gamma/\partial\mu_1)_T = [\Gamma_1 - (n_1/n_2)\Gamma_2] = \Gamma_{1(2)} \qquad (13)$$

The quantity s, the surface excess entropy, is the amount by which the entropy per unit area of surface exceeds the entropy of the same material content in the liquid phase. The surface excess of component 2 (relative to component 1), i.e., $\Gamma_{2(1)}$, is the amount by which Γ_2 exceeds the quantity of component 2 which would be associated with Γ_1 of component 1 in the liquid phase; and conversely for $\Gamma_{1(2)}$. (It will be noticed that all three quantities, s, $\Gamma_{2(1)}$, and $\Gamma_{1(2)}$ are invariant with respect to the separation of planes AB and CD in Fig. 1, provided that the separation is great enough to include in σ the whole of the layer in which composition is varying across the interface). Equation 13 is derived from the equation [similar to (10)] obtained by eliminating $\partial\mu_2/\partial x_2$ from (9). For the pure solvent we have an equation analogous to (11),

$$-(d\gamma^0/dT) = (S^\sigma/A - \Gamma_1 S_1^0) = s^0 \qquad (14)$$

It will be noticed that there has been no mention of ions, and in fact the above equations are independent of whether the solute is an electrolyte or non-electrolyte. Since a gas phase at equilibrium with a liquid phase contains no measurable concentration of ions (at ordinary temperatures) and since the interphase as a whole must be electrically neutral, the surface excess of cations must be equivalent to that of anions, and can be described as a surface excess of neutral molecules. However, there may be different distributions of cations and anions, and surface-potential measurements show that anions usually approach the surface more readily than cations. This information cannot be derived from a thermodynamic study of the surface. In contrast, in the system known as an ideal polarized electrode (37), an unbalanced surface excess of, say, anions on the electrolyte side of the interface may be countered by a corresponding deficit of electrons in the metal electrode, and the charge density in this double layer *across* the physical interface is a measurable quantity. Together with the

conjugate intensive quantity, i.e., the e.m.f. between the metal and a reversible electrode in the electrolyte phase, the charge density can be included in a thermodynamic treatment (36) of the interface. Surface excesses of individual ionic species can be derived, and, with some reasonable assumptions about the diffuse ionic layer the specific adsorption of different ions can be calculated. Nothing of this sort is at present possible for the electrolyte solution–gas interface.

2. Surface of the Pure Solvent: Temperature Dependence of Surface Tension

The surface tension of most liquids (a few metals may be exceptions) decreases with increasing temperature, indicating a positive surface excess entropy. For water at 25°C,

$$s^0 = -(d\gamma/dT) = 0.157 \text{ erg cm}^{-2} \text{ deg}^{-1}$$

One square centimeter of a monolayer of water molecules contains about 1.7×10^{-9} mole water* so that if the excess entropy were restricted to a single layer of molecules it would be equivalent to 2.18 cal deg^{-1} mole^{-1} in this layer. This is equal to the entropy increase in bulk water when its temperature is raised from 25° to 63°C. This is not a large amount and although it is probably not concentrated in one layer of water molecules it is unlikely to extend to more than two or three layers. More definite evidence of the rather abrupt transition from the liquid to the vapor phase is provided by optical studies. The ellipticity of light reflected from the surface of a liquid at the Brewsterian angle (tan^{-1} n, where n is the refractive index of the liquid) depends on the thickness of the transition layer and the way in which the refractive index changes through the layer. For an absolutely abrupt transition the ellipticity would be zero. For most liquids it is very small (39,42) and for water McBain (32) concludes that the transition layer cannot be less than 2.26 A thick but probably does not exceed this greatly. Since the thickness of a monolayer of

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* This figure is equivalent to the number of water molecules in the surface of one face of a 1-cm cube of water. The number of molecules in the cube is (6.02 × 10)/18^{23} 3.34 × 10^{22}, therefore the number on a face (3.34 × 10^{22})$^{2/3}$ 1.04 × 10^{15} molecules 1.72 × 10^{-9} mole.

water molecules is about 3 A, the implication is that the layer of intermediate densities at the surface of water is only one or two monolayers thick. This is also the region in which the greater part of the change of dielectric constant occurs since there is no reason to suppose that molecular rotation is more restricted than in the bulk (preferential orientation of dipoles near the surface seems to be small, see section III.1).

The temperature dependence of the surface tension of aqueous electrolyte solutions is very similar to that of pure water (26). Solutions of those salts such as nitrates and thiocyanates that cause a smaller increment of surface tension than usual, appear to have a smaller temperature coefficient $(-d\gamma/dT)$ than does either pure water or solutions of other 1 : 1 salts, but the available data is not of sufficient accuracy for any significant deductions to be made.

II. The Concentration Dependence of Surface Tension

1. General Considerations

Early work on the surface tension of aqueous solutions of salts showed that in general the surface tension increased approximately linearly with increasing concentration of salt (19). It was also noticed that equivalent concentrations of many different salts of the same valence type gave almost identical increments of surface tension (46). This observation suggests that the effect of low concentrations of ionic solutes on the surface tension of water may be explicable on the basis of Coulombic forces only. At higher concentrations different ions of the same charge begin to exhibit specific differences and there is a correlation with the "lyotropic series" (10). The higher an ion is in this series (i.e., the more highly hydrated), the greater the increment in surface tension it causes. The effects of the two ions present in a solution of a simple salt are roughly additive.

There are thus two main problems of interest: first, the interpretation of the surface tension of very dilute electrolyte solutions on the basis of Coulombic forces (equivalent to the Debye-Hückel theory for dilute solutions), and second, the interpretation of

specific differences at higher concentrations. For the study of both these problems, but particularly of the former, very accurate surface-tension measurements are required since the differences of surface tension are very small. The methods most frequently used in the more recent work have been the drop-weight method (14,16–18) the capillary rise method (20,21) and the maximum bubble pressure method (2,3,30,38). The most precise measurements are probably those of Jones and Ray (20,21), Long and Nutting (30), and Passoth (38). The original papers should be consulted for details of the methods. We shall proceed directly to consider the theoretical predictions for dilute solutions and the comparison of these with the experimental results.

2. Theory and Experimental Results

A. Theory for Dilute Solutions. The surface tension of very dilute electrolyte solutions, as we have remarked, appears to
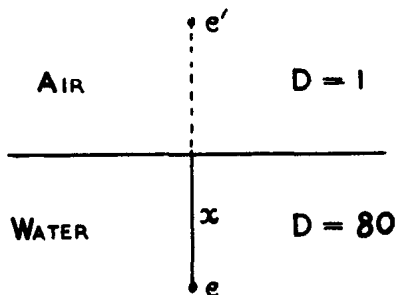

Fig. 2.

depend on concentration and valence type only and should therefore be determined by Coulombic forces alone. The first attempt to work out a quantitative theory on this basis was made by Wagner (48). A charged particle near the interface between two dielectrics, e.g., water and air, is subject to an image force tending to drive the particle from the phase of lower dielectric constant into that of higher. An ion in an aqueous solution is thus repelled from the surface. Taking the dielectric constant of the gas phase (air + water vapor) to be 1 and that of water as D, an ion of charge e at a distance x from the surface (Fig. 2) is repelled as

though by a charge e' at a distance $2x$ in a uniform medium of dielectric constant D, where

$$e' = [(D - 1)/(D + 1)]e \qquad (15)$$

In view of later approximations it is sufficiently accurate when $D = 80$ (water) to substitute 1 for $(D - 1)/(D + 1)$. The electrostatic energy of a charge e due to this image force is then

$$\int_0^\infty \frac{e^2}{D(2x)^2}\, dx = \frac{e^2}{4Dx} = W(x) \qquad (16)$$

If the concentration is c at $x \to \infty$, the concentration at x is $c \exp[-W(x)/kT]$ and the total amount desorbed per unit area of surface is

$$-\Gamma_{2(1)} = c \int_0^\infty \{1 - \exp[-W(x)/kT]\}\, dx = \infty \qquad (17)$$

This leads to an infinite increment of surface tension, a paradox which is resolved by taking into account the screening effect of the ionic atmosphere. When x is larger than the radius of the ionic atmosphere, $1/\kappa$, $[\kappa = (4\pi/DkT) \sum_i c_i e_i^2]$ the electrical image of the ionic atmosphere largely cancels that of the central ion. The image force and $W(x)$ therefore fall rapidly towards zero as x increases beyond $1/\kappa$. In the calculation of $W(x)$ for smaller values of x, a considerable mathematical difficulty arises from the dependence of κ on concentration which itself depends on x. To overcome this, Wagner made the approximation of giving κ the same value from $x = 0$ to x as it has at distance x. However, laborious numerical integrations were still required to solve the equations, and Onsager and Samaras (35) further simplified the problem by assuming κ to be constant, having the same value up to the surface as in the bulk of the solution. Expression (16) for $W(x)$ then becomes

$$W(x) = (e^2/4Dx)e^{-2\kappa x} \qquad (18)$$

which obviously decreases rapidly as x exceeds $1/\kappa$. On substituting this into (17), $\Gamma_{2(1)}$ becomes finite. By substituting into Eq. 12 the calculated value of $\Gamma_{2(1)}$, and integrating, Onsager and Samaras obtained an expression for $\Delta\gamma(=\gamma - \gamma_0)$ as the sum of a series.

Values of this sum are tabulated (35) for a range of concentrations of electrolyte in aqueous solution. The limiting law for very dilute solutions of 1 : 1 salts takes the form

$$\Delta\gamma_{298} = 1.012m \log_{10}(1.467/m) \qquad \text{dyne cm}^{-1} \qquad (19)$$

for water as solvent at 25°C. Expression 19 and also Onsager and Samaras' tabulated values are plotted in Fig. 3.
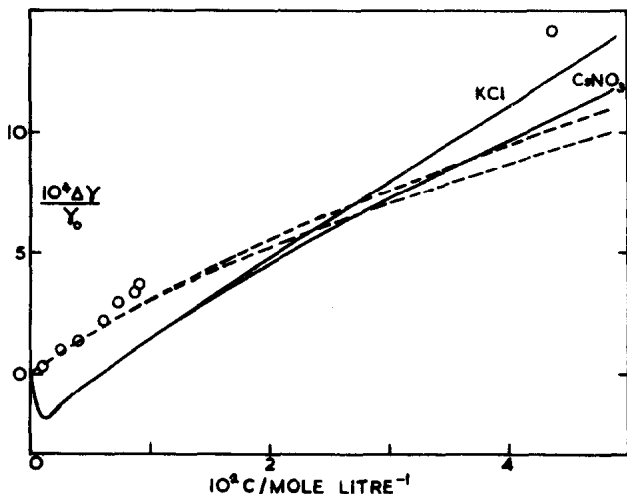

Fig. 3. Full lines: measurements of Jones and Ray; broken lines: theoretical curves calculated by Onsager and Samaras; upper curve: tabulated values; lower curve: limiting law (Eq. 19). Circles: measurements of Long and Nutting.

B. Comparison of Experimental Results with the Onsager-Samaras Equations.

In order to test the validity of the Onsager-Samaras theory, Jones and Ray (20,21) made a series of measurements of surface tension of dilute aqueous solutions of several salts. By using a highly sensitive differential capillary rise method, with a quartz capillary, they were able to make significant measurements of $\Delta\gamma/\gamma_0$ down to 0.00004, i.e., $\Delta\gamma \simeq 0.003$ dyne cm^{-1}. Their results indicated an apparent decrease of surface tension with increasing salt concentration up to about 10^{-3} equivalent per liter for all the salts they studied, followed by the normal increase at higher concentrations (curves for KCl and CsNO$_3$ are

plotted in Fig. 3). This unexpected result, which became known as the Jones-Ray effect, implies adsorption of the salt at the surface at very low concentrations followed by desorption at higher concentrations. Attempts were made to explain the phenomenon as a true surface-tension effect, by Dole (8) and Bikerman (5). However, an alternative suggestion by Langmuir (28) that it might be an instrumental error due to the finite thickness of the "wetting layer" on the inside of the capillary has since proved to be correct. In contact with a dilute aqueous solution of a non-surface-active $1:1$ salt such as KCl, a quartz surface becomes negatively charged and this gives rise to a complementary diffuse layer of charge in the adjacent solution. The thickness of this layer is related to the Debye length, $1/\kappa$, and the concentration of ions in it depends on the charge density (i.e., on the ζ potential) of the quartz surface. When a quartz capillary is wetted internally with a dilute electrolyte solution and then raised, the osmotic effect of the excess ionic strength in the diffuse layer of charge prevents the drainage of liquid from the surface when the remaining film has been reduced to a thickness comparable to $1/\kappa$. The reduction of the effective bore of the capillary by this layer should be greatest when the ionic strength is least and should diminish, with rising ionic strength, to a negligible amount when the electrolyte concentration approaches $10^{-2}\ M$. This change in the effective bore of the capillary causes a decrease in the capillary rise which is superimposed on, and at very low concentration completely obscures, the increase of rise due to increasing surface tension with increasing concentration.

Experiments designed to test the ability of Langmuir's theory to account quantitatively for the observed effects were made by Jones and Wood (22). They made careful measurements of the ζ potential of quartz in aqueous KCl at low concentrations and on the basis of Langmuir's theory calculated the thickness of the wetting layer of these solutions in a quartz capillary. Treating this as a decrement $(-\Delta r)$ in the radius of the quartz capillary used by Jones and Ray (20) they made the appropriate corrections to the latter's measurements of γ. The results are summarized in Table I. The $\Delta\gamma$'s in this table are increments in γ over that for $10^{-5}\ M$ KCl, with and without making the correction for the wetting layer in the capillary for each solution. The surface

TABLE I
Measurements of Jones and Ray Corrected for
Wetting Layer in Capillary (22)
(Internal radius of capillary = 0.0136 cm)

m (KCl)	$10^{-5}\,M$	$10^{-4}\,M$	$10^{-3}\,M$
ζ, volt	−0.148	−0.135	−0.112
$1/\kappa$, A	962	304	96.2
$-\Delta r$, A	520	450	250
$\Delta\gamma/\gamma_0$, uncorrected	—	−0.00003	−0.00018
$\Delta\gamma/\gamma_0$, corrected	—	+0.00002	+0.00002

tension of $10^{-5}\,M$ KCl may be taken as equal to that for water, within the experimental error. According to the Onsager-Samaras theory $\Delta\gamma/\gamma_0$ for $10^{-4}\,M$ and $10^{-3}\,M$ KCl should be 0.6×10^{-5} and 4.5×10^{-5}, respectively, with which the corrected experimental value of 2×10^{-5} for each solution agrees to within the probable experimental error. Thus the low concentration anomaly disappears. Similar calculations by Robinson (43) confirm this conclusion.

It has also been found possible by using other methods of measurement to obtain directly surface-tension values which exhibit no anomalous behavior at low concentrations. Long and Nutting (30) used an elegant differential form of the maximum bubble pressure method to measure surface tensions of aqueous KCl at concentrations up to $0.01\,M$. Their results are also shown in Fig. 3 and give no indication of a minimum in the γ–concentration curve. At first sight this is surprising since the inside of the capillary was wetted by the solution in the intervals between bubble formation as is usual in this method, and the effective internal diameter should then be diminished by the wetting layer as in the capillary rise method. An explanation has been put forward by Passoth (38) who used another modification of the same method. He found that if the interval between the bubbles was long (2 min) he obtained a minimum in the γ–concentration curve, while if it was fairly short (15 sec) there was no such minimum (Fig. 4). He suggested that if there is sufficient time for drainage of the liquid film in the capillary down to the limit prescribed by Langmuir's theory, then the minimum in the γ–c curve will be found, but if much less time is allowed the liquid film always reaches the same thickness determined simply by the

rate of drainage and no minimum appears. This seems to be a
probable explanation even though Long and Nutting did not
detect any dependence of bubble pressure on bubble frequency
over a limited range of the latter. The horizontal wire detachment
method [due to Lenard (29)] has been used as a high-precision
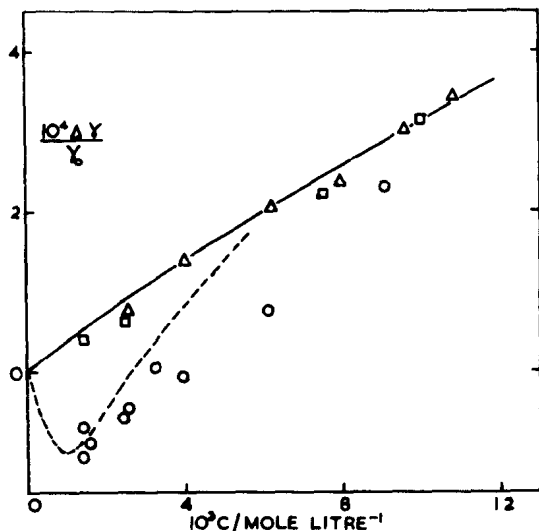differential method by Schäfer et al. (44) who also found no

Fig. 4. Full line: Onsager-Samaras equation; broken line: Jones and Ray
experimental curve for NaCl; triangles: NaCl; squares: KBr; both with bubble
interval 15 seconds; circles: NaCl, with bubble interval 2 min (From Passoth,
ref. 38).

Jones-Ray effect. This is to be expected if the Langmuir theory
is correct since a small variation of the thin film of liquid adhering
to the wire would not (even if it occurs) appreciably affect the
measured force of detachment from the liquid surface.

The correctness of Langmuir's theory and the absence of any
minimum in the true surface tension–concentration curves may
therefore be assumed. We must therefore enquire how well such
curves, without minima, are represented by the Onsager-Samaras
calculations. Reference back to Fig. 3 shows that agreement with
the results of Long and Nutting for KCl up to 0.01 M is fairly
good. At higher concentrations the curve for KCl shows

increasing deviation with increasing concentration but there is rather better agreement for $CsNO_3$. In Fig. 5 the comparison is extended up to a concentration of $0.1\ M$ and the minimum in each curve has been eliminated by extrapolating the normal part of each curve (γ increasing with concentration) back to zero concentration. The curves for KCl and NaCl (Jones and Ray's
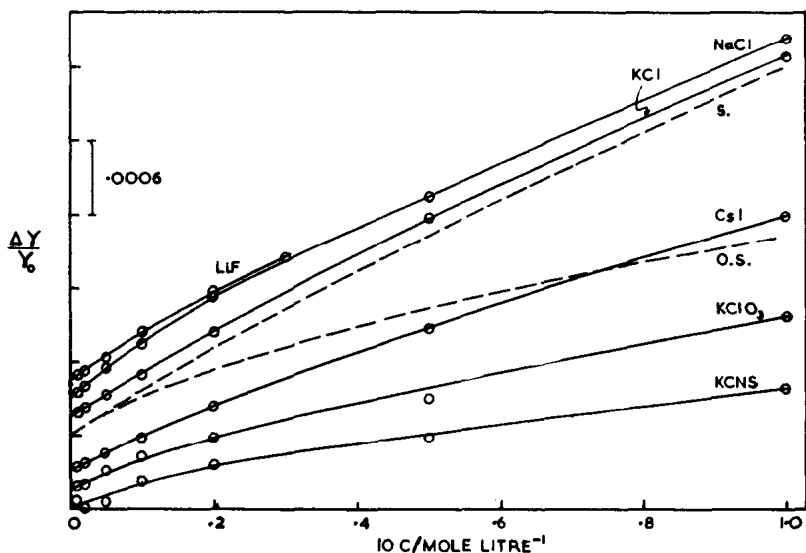

Fig. 5. Full lines and circles: Experimental results of Jones and Ray. Broken lines: upper curve, calculated by Schmutzer (ref. 45); lower curve, from Onsager and Samaras' tabulated figures.

results) also represent quite accurately the surface tension data of Schäfer et al. (44) for these two salts. It can be seen that the curve representing the Onsager and Samaras equation has an initial slope similar to that of the KCl curve but falls markedly below it at concentrations above about $0.01\ M$. (This theoretical curve is drawn from the figures tabulated by Onsager and Samaras. The limiting law, Eq. 19, falls significantly below the line drawn in Fig. 5 at concentrations above about $0.02\ M$.) The NaCl curve has a somewhat higher initial slope, which may be due to experimental error as at higher concentrations the NaCl and KCl curves almost coincide. On the other hand, the curves for $KClO_3$

and KCNS have a lower initial slope than that of the Onsager-Samaras curve.

Before considering alternative theories and attempts to obtain better agreement with experiment at higher concentrations, we shall briefly discuss the main physical facts which are omitted from the Onsager-Samaras model. In the first place, this model underestimates the electrical image forces by ignoring the increase in $1/\kappa$ as the surface is approached. If this were taken into account $\Delta\gamma$ would be increased. Second, the concept of a uniform dielectric bounded by a plane ignores the gradual decline of density and dielectric constant through a surface layer about two molecules thick (see section I.2). This decrease of dielectric constant near the boundary of the liquid phase has been cited (38,44) as causing a deficit of ions near the surface additional to that calculated in the Onsager-Samaras theory, but its net effect on the surface excess $\Gamma_{2(1)}$ is probably small.* Third, and most important, the influence of the molecular structure of the dielectric on its interaction with an ion is ignored. One effect of this which might be expected is that the reluctance of some ions to lose their first hydration shell (as indicated by the existence of hydrated ions in crystalline salts) would prevent their losing it at the surface of the solution. At the nearest approach of such ions to the surface, at least one water molecule would be retained between the ion and the gas phase. If this were true of both species of ion present in an electrolyte solution, there would be an ion-free layer at least one water molecule thick at all concentrations of the solution, which would increase $\Delta\gamma$ over the value calculated by Onsager and Samaras. On the other hand, as we have seen, some salts ($KClO_3$, KCNS) cause a $\Delta\gamma$ less than that predicted by the Onsager-Samaras theory. This can only result from adsorptive forces which oppose the various desorptive forces. The mechanism of these specific adsorptive forces is not known, but it must be related to the structure of the hydration shell of the ions concerned and the structure of the water surface. We shall discuss the question in more detail in section III.1.

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* While the lower dielectric constant lowers the number of ions in a surface layer of specified depth, the lower density of the water also means less water in the same layer. Thus both Γ_2 and Γ_1 in Eq. 12 are decreased and the effects on $\Gamma_{2(1)}$ tend to cancel.

C. Other Theoretical Approaches. A rather elaborate calculation based on the same model as that of Onsager and Samaras has been carried out by Buff and Stilbinger (6); this has yielded theoretical values of $\Delta\gamma$ which do not fall below the experimental values until higher concentrations, but the improvement is not very great. Other theories of the surface tension of aqueous electrolytes have been put forward by Oka (34), Ariyama (1), Belton (4), Schäfer et al. (44), and Schmutzer (45). Oka and Ariyama attributed the forces repelling ions from the surface entirely to the lack of ionic atmosphere on the gas-phase side of the interface. Image forces resulting from the change of dielectric constant at the interface were ignored, and this neglect must render these theories unrealistic. Belton (4), on the other hand, ignored ion–ion interactions and considered only interactions between ions and the polar molecules of the solvent. However, he assumed an arbitrary distance of closest approach of an ion to the surface, equal to 4 A, and his calculations were only directed to finding out how the "water layer" at the surface of an aqueous salt solution changed with changing salt concentration. Why there should be a 4-A water layer at the surface was not considered.

Schäfer et al. (44) developed a theory based on electrical image forces, with partial screening by the ionic atmosphere. The image forces are interpreted as a loss of (negative) hydration energy as the surface is approached. This is a legitimate interpretation and allows the authors to introduce differences for different ions by using Webb's (49) values for "effective" ionic radii and dielectric constant close to an ion. However, the theory is complicated and its value diminished by the use of adjustable parameters related to the hydration of ions and to the closest possible approach of ions to the surface. In this respect the work of Schmutzer (45) is preferable. He assumes the existence of forces repelling ions from the surface additional to those included in the Wagner-Onsager model, but represents them simply by an infinite potential barrier at a distance δ from the surface. It must be admitted that present knowledge of ion–water interactions and the surface structure of water does not justify any more detailed model. Beyond the ion-free layer of thickness δ, Schmutzer calculates the distribution of ions on the basis of electrical image forces partly screened by the ionic atmospheres, as did Onsager and Samaras. Thus the two

theories give the same limiting law for infinite dilution, when the surface layer of the solution is devoid of ions as a result of the image forces (without any special assumption about a potential barrier). For medium concentrations (order of $0.1\ M$) Schmutzer's formula is

$$\Delta\gamma = \frac{m\nu RT\delta\varphi}{1000} + \frac{kT}{32\pi\delta^2}\,I_0(2\delta\kappa) \qquad (20)$$

where m is the molality of the solution, ν the number of ions per molecule of solute, R and k the gas constant per mole and per molecule, respectively, and φ is the osmotic coefficient of the solution. $I_0(2\delta\kappa)$ is an integral function which Schmutzer has evaluated and tabulated for a series of values of $2\delta\kappa$ (κ is the reciprocal of the radius of the ionic atmosphere).

The first term on the right-hand side of Eq. 20 is the surface-tension increment due to the ion-free layer of thickness δ. This is easily demonstrated. Suppose that below the ion-free layer the solution is uniform, therefore there is a surface excess of water ($\Gamma_{1(2)}$) equal to the quantity in this layer. The volume of the layer is δ cm³ per square centimeter. Alternatively this layer may be regarded as y monolayers of water molecules where y need not be an integer. Thus, taking the molecular volume of water as 18 cm³, and using also the figure given in the footnote in section I.2,

$$\Gamma_{1(2)} = \delta/18 = 1.72 \times 10^{-9}\,y \text{ moles cm}^{-2}$$

The activity of water in the solution is related to the molal osmotic coefficient, φ, by

$$\ln a_{H_2O} = -(18\nu m/1000)\varphi$$

so that

$$d\mu_{H_2O} = -(18RT/1000)\,d(\nu m\varphi)$$

Thus Eq. 13 becomes

$$\frac{\partial\gamma}{\partial(\nu m\varphi)} = \frac{18RT}{1000}\,\Gamma_{1(2)} = 0.248 \times 10^8\delta = 0.767y$$

$$\text{dyne cm}^{-1}/(\text{mole kg}^{-1}) \qquad (21)$$

a result which we shall make use of later. If δ is constant we have

$$\Delta\gamma = (RT\delta/1000)\nu m\varphi \qquad (22)$$

which is identical with the first term on the right-hand side of (20).