

Calculation of surface tension of salt solutions: effective polarizability of solvated ions

Robert A. Stairs

Abstract: The Onsager-Samaras version of Wagner's theory of surface tension of solutions of 1:1 salts has been modified to include ion-induced dipole terms in the image potential. Effective solvated ionic polarizabilities are used, which are large and negative owing to local dielectric saturation around the ions. The modified theory agrees with the order of magnitude of the variation among various alkali halides (e.g., $\Delta\sigma$ for 0.1 molar aqueous KI is about 70% of the corresponding value for KCl). Polarizabilities were estimated from Hasted's dielectric decrements.

Key words: surface tension, salt solutions, symmetric electrolytes, effective polarizability, theory.

Résumé : On a modifié la version de la théorie de Wagner, élaborée par Onsager et Samaras, de la tension superficielle des solutions des sels 1 : 1, par l'addition à l'expression pour l'énergie potentielle due à l'image d'un terme représentant l'énergie charge/dipolaire. On a employé des polarisabilités effectives qui sont grandes et négatives, à cause de la saturation diélectrique près de l'ion solvaté. La théorie ainsi modifiée est en accord approximatif avec la variation entre divers sels. (Par exemple, l'élévation de la tension superficielle de l'eau dans une solution 0,1 molaire par le IK est de 70% de celle par le KCl.) On a estimé les polarisabilités à partir des décroissements diélectriques de Hasted.

Mots-clés : tension superficielle, solutions de sels, électrolytes symétriques, polarisabilité effective, théorie.

[Traduit par la rédaction]

Simple salts, when dissolved in a molecular solvent, raise the surface tension, σ , by small amounts (in contrast with surface-active agents, which may depress the surface tension substantially at very low concentrations). The magnitude of the increase depends upon the charge and size of the ions and on the nature of the solvent.

The functional form of the dependence of $\Delta\sigma$ ($= \sigma - \sigma_0$) on concentration is very uncertain, especially the approach to zero concentration. Most data (1) for aqueous solutions are at concentrations above 0.1 mol L⁻¹. Other properties of strong electrolyte solutions, such as equivalent conductivity and the logarithm of the activity coefficient, which are explained by the Debye-Hückel theory or theories based on it, are represented by equations having a leading term in the square root of c . It would not be surprising if surface tension was similar in this respect:

$$[1] \quad \Delta\sigma = A_0\sqrt{c} + Bc$$

The leading constants, corresponding to A_0 , for the other properties depend only on charge type and on ϵT to a negative power. To see whether this was the case with surface tension also, data for half a dozen alkali halides in five solvents were

fitted (2) to equations of the above form, and the values of A_0 were then fitted to an equation of the form:

$$[2] \quad A_0 = a + b/\epsilon T$$

with $a = -2.4 \times 10^{-6} \text{ J m}^{-1/2} \text{ mol}^{-1/2}$ and $b = 1.83 \times 10^7 \text{ J m}^{-1/2} \text{ mol}^{-1/2} \text{ K}^{-1}$. The coefficient of determination (a statistic that is unity for a perfect fit and zero for uncorrelated data) was only 0.64.

Theories

Published theories fall into three groups: (i) direct calculations (typified by those of Oka (3) and Ariyama (4)) of the work of separation at a surface originally in the interior of the solution to make two new surfaces; (ii) calculations of the depletion ("negative adsorption") of electrolyte in a surface layer, followed by use of the Gibbs adsorption equation (see below); (iii) calculations starting from a radial distribution for the ions, and proceeding by statistical-mechanical methods (5, 6). The main theories in the second group are (a) those of Wagner (7) and Onsager and Samaras (8) ("WOS"), modified by later authors (9, 10), and (b) that of Péres Masiá and co-workers (11, 12).

Binary mixtures of nonelectrolytes exhibit surface tensions that are lower than the values calculated with an assumption of additivity on a molar basis, i.e., :

$$[3] \quad \sigma < \sigma_1 x_1 + \sigma_2 x_2$$

where σ represents the surface tension of the solution, σ_i is

Received November 21, 1994.

R.A. Stairs.¹ Department of Chemistry, Trent University, Peterborough, ON K9J 7B8, Canada.

¹ Telephone: (705)748-1201. Fax: (705)748-1625. E-mail: rstairs@trentu.ca

the surface tension of pure component **i** and x_i is its mole fraction. The reason for this is that the surface tension, which is the same as the surface free energy, is reduced by an excess of the component with the lower surface free energy appearing in the surface layer. Gibbs showed how to relate the surface excess ("adsorption") of one component to the decrease in the surface tension, through the Gibbs Adsorption Equation (13), a form of which is eq. [4]:

$$[4] \quad d\sigma/d\ln a_2 = -RT\Gamma_2$$

Here σ is as defined above, a_2 is the activity of component **2**, R is the gas constant, T the absolute temperature, and Γ_2 is the surface excess of component **2**. The definition of Γ_2 is somewhat dependent on the placing of an arbitrary plane that marks the geometrical surface (the real surface being actually a somewhat diffuse region). Gibbs showed that for dilute binary solutions it is always possible to place this plane so that the surface excess is equal to the integral of the local excess of component **2** (the solute) from the arbitrary plane into the body of the solution, to infinity, eq. [5]:

$$[5] \quad \Gamma = \int_0^\infty [c(x) - c(\infty)] dx$$

where x is the distance from the surface into the solution, and $c(x)$ and $c(\infty)$ are the concentrations at x and ∞ ("bulk").

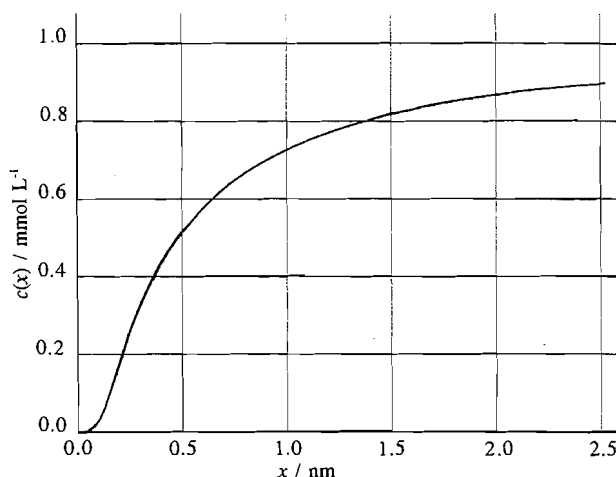
Where the solute is a strong electrolyte, each of the ions interacts with the surface, independently of the others in the limit of extreme dilution. By treating the surface as a plane that divides space into two regions, one the solvent, with electric permittivity ϵ , and the other the gas or vapour, with a permittivity essentially equal to the permittivity of free space, ϵ_0 , it may be shown (14) that an ion of charge ze will be subject to a repulsive force equal to that which would be exerted by a charge of magnitude $ze(\epsilon - \epsilon_0)/(\epsilon + \epsilon_0)$ at the place where the image of the ion would be were the surface a mirror, with the permittivity everywhere equal to ϵ . This results in the ion having an x -dependent contribution to its potential energy, given by eq. [6],

$$[6] \quad W = fe^2/16\pi\epsilon x$$

where $f = (\epsilon - \epsilon_0)/(\epsilon + \epsilon_0)$, the ratio of the image charge to the real charge. The extra factor 4 in the denominator arises because, in the integration of the force to obtain the potential energy, one must take account of the motion of the image as the ion is moved.

The dependence of concentration on distance from the surface is then obtained as $c(x) = c(\infty)\exp(-W/kT)$, where k is Boltzmann's constant. WOS show that this leads to Γ 's being negative and infinite. At any finite concentration of electrolyte, however, the range of the Coulombic force of repulsion (the "image force") should be limited by the effect of the ionic atmosphere, being attenuated by the Debye-Hückel factor $\exp(-\kappa r)$. The radial coordinate r causes intractable mathematical complications; it was replaced by Wagner by a new coordinate parallel to x , and by Onsager and Samaras by $2x$ (because the distance from the image to the real ion is $2x$). The Debye-Hückel reciprocal length κ is not constant in the region of the solution where the concentration is not uniform. Onsager and Samaras argue that the value corresponding to

Fig. 1. Distribution of an ionic solute near the solution surface. The bulk concentration is $1.000 \text{ mmol L}^{-1}$. The local concentration is plotted as a function of the distance from the surface, x ; the quantity $-\Gamma$, which is the depletion (negative adsorption) of the solute, is the area between the curve and the horizontal line at $c = 1 \text{ mmol L}^{-1}$. It is equivalent to total exclusion of solute from a surface layer about 0.8 nm thick. (Recalculated after Onsager and Samaras's Fig. 2 (8).)



the bulk concentration may be used without serious error. With these simplifications, they obtain a dependence of concentration on distance from the surface of the form shown in Fig. 1 (redrawn from part of Onsager and Samaras's Fig. 2). The area between the curve and the horizontal line at $c(\infty)$ is the quantity $-\Gamma$. Treatment of the liquid as a continuous dielectric should break down within molecular distances from the geometrical surface. Fortunately this is just the region that is essentially salt free. Integration of the Gibbs equation then gives $\sigma(a)$ or $\sigma(c)$.

Pérez Masía and co-workers (11, 12) begin by calculating the Born solvation energy of the ions, and then the loss of solvation due to truncation of the solvation sphere by the surface. They then proceed to calculate $c(x)$ and $-\Gamma$ essentially as WOS, except that they explicitly calculate the effect of the difference in the solvation of the cation and anion. Any difference in the degree of repulsion from the surface creates an electrical double layer; this gives rise to an additional effect that they calculate through the Lippman-Helmholtz equation:

$$[7] \quad \left(\frac{\partial \sigma}{\partial E} \right)_{T,p,n} = - \left(\frac{\partial Q}{\partial A} \right)_{T,p,n} = -q$$

where E is the surface potential, and q is the surface charge density, defined by the middle term. The subscripts indicate that the derivatives are at constant temperature, pressure and composition. This additional effect (which would lead to a decrease in surface tension) is small when the ions have equal and opposite charges. It was neglected by WOS, and is neglected in **this work**.

All of these theories predict concentration dependence that is either linear for strong electrolytes or slightly concave towards the concentration axis. The curvature arises from two sources: (a) at higher concentrations from ion pairing (e.g.,

Oka (3b): he includes a factor α for the degree of dissociation) or from the activity coefficient (e.g., WOS) and (b) at low concentrations from a term proportional to $-c \ln(c)$ (WOS and successors). Nichols and Pratt (15) show that in their application of the WOS approach to interfacial tension between two liquids the leading term may have the form either $-c \ln(c)$ or $c^{1/2}$, depending on the difference in the degree of repulsion from the surface between the anion and the cation, especially if the salt shows some solubility in both liquids. Unfortunately the effect is so small that these two forms of dependence on c are experimentally indistinguishable.

In reviewing these various theories from the point of view of an engineer seeking smoothed or estimated values, Horvath (16) concludes that for lower concentrations (below about 0.1 mol L^{-1}), WOS best represents the data. (He prefers Schmutzer (5), Buff–Stillinger (6), or Molyneux (17) at higher concentrations, although their derivations are also for very dilute solutions.) The chief problem seems to be that WOS underestimate the effect of ionic size. Onsager and Samaras themselves also say that they slightly underestimate the magnitude of the main effect (8).

Calculations

Onsager and Samaras, in calculating the “image” force, treat the ions as having no properties except charge and size, but, without elaborating, they mention the possibility of including polarizability. M.J. Sienko, in about 1953, suggested in conversation² that we should explore the addition of polarizability to see whether it might account for ionic size effects more realistically. The calculation seemed too difficult, and, except for a rough order-of-magnitude estimate, we were unable to pursue the problem at that time. The present paper is the belated fruit of Sienko’s suggestion.

To allow for the size of the ions, WOS modify the potential energy of the ion by introducing the Debye–Hückel distance of closest approach, a , and arrive at the form (their eq. 19):

$$[8] \quad W(x) = \left(\frac{\exp(\kappa a)}{1 + \kappa a} \right) \left(\frac{fz^2 e^2}{16\pi\epsilon x} \right) \exp(-2\kappa x)$$

(where x is the distance from the surface, a and κ are the Debye–Hückel distance of closest approach and ionic-atmosphere parameter, ϵ is the permittivity, z is the charge number, e is the elementary charge, and we have here restored the omitted f , the ratio of the image to the real charge: $(\epsilon - \epsilon_0)/(\epsilon + \epsilon_0)$).

We now add a term, the sum of two identical terms, for the potential energy W_μ due to the force (i) between the image charge and the induced dipole at the real ion and (ii) between the image of the induced dipole and the real charge. To obtain this term, consider the local field, E , which is (in one dimension) the derivative of the potential due to the image:

$$[9] \quad E = \frac{d\phi}{dx} = \frac{d}{dx}(W(x)/ze)$$

The induced dipole moment, μ , is equal to the product of the

local field and the polarizability α . The force on the dipole is given by the product of the dipole moment and the derivative of the field:

$$[10] \quad F_\mu = \frac{dE}{dx} \alpha E = \alpha \frac{d^2\phi}{dx^2} \frac{d\phi}{dx}$$

and the potential energy W_μ due to this force is:

$$[11] \quad W_\mu = -\alpha \int \frac{d\phi}{dx} \frac{d^2\phi}{dx^2} dx = -\alpha \int \frac{d\phi}{dx} d\left(\frac{d\phi}{dx}\right) = -\frac{\alpha}{2} \left(\frac{d\phi}{dx}\right)^2$$

(The constant of integration is taken to be zero, the force and the potential energy both being zero at great distance.)

By itself, this term, which is attractive if α is positive, causes the potential energy of an ion at the surface to be large and negative, so the area Γ again becomes infinite and positive. Since the effective polarizability of a solvated ion is always negative, however (see below), the area remains finite and negative. A term representing the (induced) dipole–dipole potential was originally added. Since the range of the corresponding force is short, it serves only to reduce further the concentration very close to the surface, from which the solute is nearly totally excluded by the other forces. Its effect is therefore negligible.

The final form of the potential function is now:

$$[12] \quad W(u) = \frac{\exp(\kappa_0 a c^{1/2})}{1 + \kappa_0 a c^{1/2}} F_1(u) c^{1/2} - 2 \left\{ \frac{\exp(\kappa_0 a c^{1/2})}{1 + \kappa_0 a c^{1/2}} \right\}^2 F_2(u) c^2 \alpha$$

where $u = 2\kappa x = 2\kappa_0 c^{1/2} x$ (writing κ_0 for $\kappa/c^{1/2}$), and

$$[13] \quad F_1 = \frac{fz^2 e^2 \kappa_0 \exp(-u)}{2\epsilon u}$$

$$F_2 = \left\{ \frac{2\kappa_0(1+u)F_1(u)}{zeu} \right\}^2$$

Then the concentration as a function of distance from the surface:

$$[14] \quad c(u) = c(\infty) \exp\left(\frac{-W(u)}{kT}\right)$$

is used to obtain the adsorption:

$$[15] \quad -\Gamma = \int_0^\infty (c(\infty) - c(u)) dx = 2\kappa \int_0^\infty (c(\infty) - c(u)) du$$

followed by integration of the Gibbs equation, eq. [4], to obtain $\Delta\sigma(c)$. Corrections for the activity coefficient were made following Onsager and Samaras (8). They state that the effect of the added term linear in ionic strength to the extended Debye–Hückel equation makes little difference. By the use of Davies’s approximation (18) to the extended Debye–Hückel equation for aqueous solutions at 25°C :

$$[16] \quad -\log_{10} f_{\pm} = \frac{z^2}{2} \left(\frac{1}{1 + I^{-1/2}} - 0.3I \right)$$

² M.J. Sienko, private communication, 1953.

where I is the ionic strength in mol/L, we found that it does indeed make a difference at concentrations above 0.1 mol L⁻¹ for 1:1 electrolytes; presumably it is even more important with ions of higher charge.

Polarizability

We have not yet discussed the choice of the values for the polarizabilities of the solvated ions. Hasted, Ritson, and Collie (19) have considered this problem and have made (very difficult!) measurements of the effect of dissolved salts on the permittivity of water, in the limit of low frequency, expressing the results in the form:

$$[17] \quad \epsilon = \epsilon_s + \delta c$$

The factor δ is called the "dielectric decrement," for the effect of the ions is to strongly orient the solvent molecules in their vicinity, much reducing their freedom to respond to an applied field, and so decreasing ϵ below the solvent value, ϵ_s . The measurements were made at concentrations from 0.5 molar upwards and extrapolated to zero concentration. The authors make a somewhat arbitrary division of the observed values between cation and anion, and report for univalent ions: H⁺ -17, Li⁺ -11, Na⁺ -8, K⁺ -8, Rb⁺ -7, F⁻ -5, Cl⁻ -3, I⁻ -7, and OH⁻ -13 (all ± 0.5) L mol⁻¹. The relative magnitudes accord more or less with expectation, those for the cations diminishing as the radius increases, a trend that seems to be followed also by fluoride and chloride. Iodide seems to be anomalous. That H⁺ and OH⁻ show the largest effects in their respective series is not surprising, considering their unusually large mobilities in water and their special structural relation to that solvent.

To translate the dielectric decrement into effective polarizability, we use the mixing rule for a dilute suspension of spheres of permittivity ϵ_1 in a medium of permittivity ϵ_m , eq. [18] (20):

$$[18] \quad \epsilon = \epsilon_m + 1.5\phi_2(\epsilon_1 - \epsilon_m)$$

(Here ϕ_2 is the volume fraction of the suspended spheres.) Writing the volume fraction ϕ_2 in terms of the molar concentration c , and noting that one mole of a symmetrical electrolyte contains two moles of particles (eq. [19]),

$$[19] \quad \phi_2 = 2Lv c$$

(v is the volume of a sphere and L is Avogadro's constant), we obtain eq. [20]:

$$[20] \quad \epsilon = \epsilon_m + 3Lv(\epsilon_1 - \epsilon_m)c$$

Bleaney and Bleaney (21) express the polarizability of such a suspended sphere by eq. [21]:

$$[21] \quad \alpha = \frac{3}{4\pi} \frac{\epsilon_m(\epsilon_1 - \epsilon_m)v}{(\epsilon_1 + 2\epsilon_m)}$$

Eliminating the volume of the spheres between eqs. [20] and [21], we obtain eq. [22]:

$$[22] \quad \epsilon = \epsilon_m + 4\pi L \frac{(\epsilon_1 + \epsilon_m)}{\epsilon_m} \alpha c$$

which, by comparison with the Hasted equation (eq. [17]), allows us to write:

$$[23] \quad \bar{\alpha} = \frac{1}{4\pi L} \frac{\epsilon_m}{(\epsilon_1 + 2\epsilon_m)} \bar{\delta} = G\bar{\delta}$$

The bars are added to indicate that the properties δ and α refer to averages of the properties of the two ionic species. The numerical value of the proportionality constant G is 6.52×10^{-26} mol in aqueous solutions at 25°C, taking $\epsilon_m = 78.304$ ϵ_0 and assuming $\epsilon_1 = 2\epsilon_0$, close to the "optical" value. (The Hasted values of δ are in L mol⁻¹, and should be expressed in m³ mol⁻¹ to obtain polarizabilities in m³. The value for a salt is the average, not the sum, of the ionic values.)

Results and discussion

The calculated values of $\Delta\sigma$ ($= \sigma - \sigma_0$) for concentrations from 0.0004 to 0.100 molar for uni-univalent electrolytes with mean effective ionic polarizabilities from zero to -2.0 nm³ are listed in Table 1. For $\alpha = 0$ they are in close (though not exact) agreement with those calculated by Onsager and Samaras (8). Figure 2 shows the results of this work plotted as $\Delta\sigma/c$ vs. $\log_{10} c$. The lowest curve is for $\alpha = 0$. A few of Onsager and Samaras's calculated values are shown: their simplest calculation, ignoring the activity coefficient and the size of the ions, as squares, and their full calculation as crosses. The small differences are due to slightly different values of the fundamental constants used, slightly different values (22)³ for ϵ and (following Bravina (23) the restoration of the factor $(\epsilon - \epsilon_0)/(\epsilon + \epsilon_0)$ in the magnitude of the image charge, which WOS omit. The circles represent very careful measurements by Long and Nutting (24) on KCl solutions. As noted above, they are somewhat higher than the calculated values, except at the lowest concentrations, where Long and Nutting suggest that they may not have quite eliminated the Jones and Ray effect (25).⁴ The upper curves represent the results of this work with α varied, plotted in the same fashion. Values of $-\alpha$ used were 0.5, 1.0, 1.5, and 2.0 nm³. (cf. argon: $\alpha = 0.00166$ pm³.) The value of $-\alpha$ required to reproduce the experimental results for KCl is greater than 2 nm³. The additional effect, $\sigma(\alpha) - \sigma(0)$ at $c = 0.100$ mol L⁻¹ is closely proportional to $(-\alpha)^{1/2}$. The value $-\alpha = 0.36$ nm³ corresponds to $\delta = -5.5$ L mol⁻¹ for KCl (Hasted (20), p. 140).

It appears that the present theory using these effective polarizabilities is able to predict only very approximately the effect of ion size differences on surface tension for 1:1 salts, as represented by the alkali halides. There also remain some puzzles, the chief of which is the behaviour of strong acids. The Hasted dielectric decrement value for HCl is -10 L mol⁻¹, which translates to an effective polarizability of -1.3

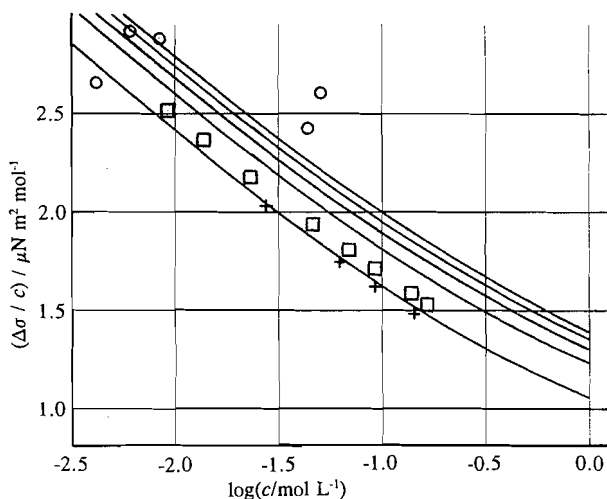
³ For temperatures other than 298 K, quadratically smoothed values were used.

⁴ The Jones-Ray effect consists of an apparent depression of the surface tension of salt solutions at very low concentrations, as measured by the method of capillary rise. Langmuir's explanation of the effect as due to the electrical double layer at the glass-solution interface (26) has been generally accepted.

Table 1. Surface tension increment divided by concentration of solutions of 1:1 salts in water, for various values of polarizability, $\alpha(\text{nm}^3)$.

$c(\text{mol L}^{-1})$	$\log(c)$	α :	$(\Delta\sigma/c)/(\mu\text{N m}^2 \text{mol}^{-1})$				
			0	-0.5	-1.0	-1.5	-2.0
0.000 40	-3.4		3.6138	3.7900	3.8688	3.9271	3.9748
0.000 63	-3.2		3.4233	3.6000	3.6789	3.7373	3.7853
0.001 00	-3.0		3.2345	3.4117	3.4909	3.5496	3.5975
0.001 58	-2.8		3.0477	3.2256	3.3051	3.3638	3.4119
0.002 51	-2.6		2.8633	3.0420	3.1218	3.1808	3.2290
0.003 96	-2.4		2.6816	2.8613	2.9414	3.0006	3.0490
0.006 31	-2.2		2.5032	2.6840	2.7645	2.8240	2.8726
0.010 00	-2.0		2.3286	2.5108	2.5917	2.6513	2.7001
0.015 85	-1.8		2.1585	2.3421	2.4234	2.4834	2.5322
0.025 12	-1.6		1.9937	2.1788	2.2604	2.3204	2.3694
0.039 81	-1.4		1.8349	2.0215	2.1035	2.1635	2.2123
0.063 10	-1.2		1.6831	1.8712	1.9531	2.0129	2.0614
0.100 00	-1.0		1.5393	1.7284	1.8100	1.8694	1.9173
0.158 49	-0.8		1.4045	1.5940	1.6747	1.7331	1.7802
0.251 19	-0.6		1.2797	1.4683	1.5477	1.6048	1.6505
0.398 11	-0.4		1.1657	1.3519	1.4291	1.4840	1.5279
0.630 96	-0.2		1.6034	1.2447	1.3188	1.3713	1.4129
1.000 00	0.0		0.9732	1.1468	1.2168	1.2658	1.3044

Temperature 298.15 K, dielectric constant 78.304.

Fig. 2. Surface tension divided by concentration for solutions of 1:1 electrolytes in water at 25°C, plotted against $\log(c/\text{mol L}^{-1})$. The curves are calculated (this work) for values of the mean polarizability of the solvated ions (from the lowest curve upwards): $\alpha = 0, -0.5, -1.0, -1.5, -2.0 \text{ nm}^3$. The plotted points are (○) experimental (KCl, Long and Nutting (24)); (+) Onsager and Samara's simplest calculation; (□) Onsager and Samara's full calculation (8).

nm^3 , and predicts a surface tension increment higher than for any of these salts. Experimental values are much lower, in fact slightly negative (1). Some structural or other special effect arising in the surface from the close relation of the hydronium ion to water must be operating. Among the alkali halides, Hasted's values of δ do not correlate very well with other properties that would be expected to show similar

trends with changes in ionic radii (e.g., entropies of solvation, viscosity B coefficients). The value of δ for KI is more negative (-8) than that for KCl (-5), but measured surface tension increments⁽¹⁾ are nearly 30% smaller.

The effects of variation of temperature, and of independent variation of the temperature, the permittivity, and the ionic charge (symmetric electrolytes only) were explored. The nature of the solvent might be expected to appear, given the electrostatic basis of the calculation, as proportionality to the permittivity to some negative power. Available data (27) do not give this much support. Good data for nonaqueous solvents are hard to find. Part (a) of Table 2 lists calculated values of the relative increment of surface tension for 1:1 salts at several concentrations and at several temperatures. Part (b) of the same table lists the results of similar calculations, but with the relative permittivity ("dielectric constant," $D = \epsilon/\epsilon_0$) fixed at the value appropriate to 298 K. In Part (c) the temperature is fixed at 298 K, with the dielectric constant varied from 60 to 100. The last column of Table 2(b) lists the values of the slopes of plots of the calculated values as $\log(\Delta v/c)$ vs. $\log(T)$. The temperature effect appears to work mainly indirectly, through the temperature dependence of the permittivity, the factor RT in the Gibbs equation and the Boltzmann factor $\exp(-W/kT)$ having contrary effects. The slopes in Table 2(b) show the near-cancellation of the direct temperature effects. Part (c) of Table 2 shows the result of varying the dielectric constant while keeping T constant. The last column, analogous to that in Part (a), shows that the effect depends approximately on D^{-1} , in the range explored.

The dependence on charge type is curious. I naïvely expected dependence on the charge as z or z^2 , and proportionality to the number of ions of each kind. This would lead to the effects of, e.g., LiCl, BaCl₂, and MgSO₄ being in the ratios 1:2:2 (if proportional to z) or 1:3:4 (if z^2). In

Table 2. Surface tension increment divided by concentration ($\Delta\sigma/c$) in $\mu\text{N m}^2 \text{mol}^{-1}$ (identical with $\text{dyne cm}^{-1}/\text{mol L}^{-1}$), calculated for solutions of 1:1 electrolytes in water (polarizability neglected).

(a) Effect of temperature.

$c(\text{mol L}^{-1})$	$\log(c)$	$\Delta\sigma/c$				
		$T(\text{K}): 273.15$	278.15	288.15	298.15	303.15
0.0001	-4.0	3.7308	3.8186	4.0012	4.1930	4.2923
0.0010	-3.0	2.8833	2.9502	3.0891	3.2345	3.3097
0.0100	-2.0	2.0812	2.1285	2.2264	2.3286	2.3813
0.1000	-1.0	1.3800	1.4106	1.4737	1.5393	1.5730
1.0000	0.0	0.8730	0.8922	0.9320	0.9732	0.9944
D^a		87.742	85.766	81.947	78.304	76.548

^aDielectric constant ($= \epsilon/\epsilon_0$) from Parsons (22) (smoothed).

(b) Effect of temperature with dielectric constant fixed at 78.304.

$\log(c/M)$	$T(\text{K}): 273.15$	$\Delta\sigma/c$				Slope ^a
		278.15	288.15	298.15	303.15	
-4.0	4.2648	4.2501	4.2212	4.1930	4.1792	-0.195
-3.0	3.2675	3.2609	3.2477	3.2345	3.2279	-0.117
-2.0	2.3300	2.3300	2.3295	2.3286	2.3280	-0.009
-1.0	1.5233	1.5268	1.5333	1.5393	1.5421	0.117
0.0	0.9612	0.9637	0.9685	0.9732	0.9755	0.142

^aSlope of a plot of $\log(\Delta\sigma/c)$ vs. $\log(T)$.

(c) Effect of dielectric constant at fixed temperature, 298.15 K.

$\log(c/M)$	$D:$	$\Delta\sigma/c$				Slope ^a
		60	70	80	90	
-4.0	5.7150	4.7814	4.0885	3.5559	3.1350	-1.1853
-3.0	4.3160	3.6567	3.1589	2.7709	2.4608	-1.0161
-2.0	3.0166	2.6009	2.2793	2.0235	1.8155	-1.0104
-1.0	1.9292	1.6955	1.5107	1.3607	1.2364	-0.8879
0.0	1.2197	1.0700	0.9557	0.8650	0.7909	-0.8466

^aSlope of plot of $\log(\Delta\sigma/c)$ vs. $\log(D)$.

aqueous solution at concentrations above 1 mol L^{-1} they are actually (28) in the ratios 1:1.8:1.3, which suggest a dependence on $z^{1/2}$, approximately, not obviously predicted by any current theory. The effect of ionic charge calculated here is surprising, in that it is strongly concentration dependent (see Table 3). At 1 mol L^{-1} the ratio of the surface tension increments predicted for 2:2 to 1:1 salts is about 1.9, which may be compared to the experimental value of about 1.3 cited above. At $0.0001 \text{ mol L}^{-1}$ the ratio is nearly 5. The reason for this strange behaviour relates to the two influences of z on the results: at the lowest concentrations the repulsive force is of long range and depends on z^2 , while at higher concentration the range of the force is limited by the ionic atmosphere, so the thickness of the layer of solution depleted in solute decreases as z increases. Thus the effect of increasing z is to increase $-\Gamma$ at low concentrations, but

Table 3. Surface tension increment divided by concentration, calculated for solutions of symmetric electrolytes in water: effect of ionic charge.

$\log(c/M)$	$ z :$	$\Delta\sigma/c$		
		1	2	3
-4.0		4.1930	20.0778	44.5752
-3.0		3.2345	13.4571	26.4473
-2.0		2.3286	7.9712	13.2374
-1.0		1.5393	4.0431	5.1603
0.0		0.9732	1.8622	1.6056

Temperature 298.15 K, dielectric constant 78.304, polarizability zero.

ultimately to decrease it at high concentrations. Note the behaviour of $\Delta\sigma/c$ for $z = 2$ and 3 in Table 3.

In conclusion, it should be pointed out that comparison of these and other theoretical calculations of surface tension of electrolyte solutions with experiment is difficult owing to the paucity of data for sufficiently dilute solutions. The present theory and all the other theories cited here were derived using assumptions that are most appropriate at very low concentrations, while the data mostly refer to concentrations much above 0.1 molar. Trustworthy data for nonaqueous systems in any concentration range are especially rare.

Acknowledgements

The author acknowledges with gratitude the hospitality and opportunity for fruitful discussion afforded by Professor A. D. Buckingham and other members of the Department of Chemistry at Cambridge University and early assistance with programming by Carol-Ann Lugtigheid. Thanks are also due to K. B. Oldham for kindly reading and commenting on an early draft of the manuscript. The work was supported by Trent University with funds provided by the Natural Sciences and Engineering Research Council of Canada.

References

1. (a) International critical tables. Vol. IV. McGraw-Hill, New York and London. 1928. pp. 463 ff; (b) Landolt-Börnstein, 1927; 5th ed. Springer-Verlag, Berlin. Edited by W.A. Roth and K. Scheel. 1927; 6th ed. Edited by K. Schäfer and E. Max. Springer-Verlag, Berlin. 1956; (c) W.D. Harkins and H.M. McLaughlin. J. Am. Chem. Soc. **47**, 2083 (1925); (d) F. DeBlock. Bull. Sci. Acad. R. Belg. **11**, 333 (1925); (e) P.P. Kosakevich, Z. Phys. Chem. (Leipzig), **133**, 1 (1928); (f) H. Falkenhagen and E. Schmutzer. Naturwissenschaften, **42**, 92 (1955); (g) C. Salceanu. C.R. Hebd. Seances Acad. Sci. **253**, 862 (1961); (h) Tsv. Tonchev and G. Popov. Nauchni Tr. Vissh. Pedagog. Inst. Plovdiv, Mat. Fiz. Khim. Biol. **8**, 93 (1970); (i) K. Johansson and J.C. Erikson. J. Colloid Interface Sci. **49**, 469 (1979).
2. R.A. Stairs, W.T. Rispin, and R.C. Makhija. Can. J. Chem. **48**, 2755 (1970).
3. S. Oka. Proc. Physico-Math. Soc. Jpn. (a) **14**, 233 (1932); **14**, 527 (1932); **14**, 649 (1932); (b) **15**, 407 (1933).
4. K. Ariyama. Bull. Chem. Soc. Jpn. **11**, 687 (1936); **12**, 32 (1937).
5. E. Schmutzer. Z. Phys. Chem. (Leipzig), **204**, 131 (1956).
6. F.P. Buff and F.H. Stillinger, Jr. J. Chem. Phys. **25**, 312 (1956).
7. C. Wagner. Phys. Z. **25**, 474 (1924).
8. L. Onsager and N.N.T. Samaras. J. Chem. Phys. **2**, 529 (1934).
9. V.E. Bravina. Zh. Eksp. Teor. Fiz. **33**, 1065 (1957); Dokl. Akad. Nauk SSSR, **120**, 381 (1958); **120**, 815 (1958).
10. T.L. Croxton and D.A. McQuarrie. Mol. Phys. **42**, 141 (1981); T.L. Croxton, D.A. McQuarrie, G.N. Patey, G.M. Torrie, and J.P. Valleau. Can. J. Chem. **59**, 1998 (1981); T.L. Croxton and D.A. McQuarrie. J. Phys. Chem. **87**, 3407 (1983).
11. A. Pérez Masiá. An. R. Soc. Esp. Fis. Quim. Ser. A: **50**, 5 (1954); **54B**, 629 (1958).
12. Kl. Schäfer, A. Pérez Masiá, and H. Jüntgen. Z. Elektrochem. **59**, 425 (1955).
13. J.W. Gibbs. Reprinted in The collected works of J. Willard Gibbs. Yale U. Press, New Haven, Conn. 1948.
14. R.K. Wangsness. Electromagnetic fields. Wiley, New York. 1979. p. 204.
15. A.L. Nichols and L.H. Pratt. J. Chem. Phys. **80**, 6225 (1984).
16. A.L. Horvath. Handbook of aqueous electrolyte solutions. Ellis Horwood, Chichester. 1985.
17. F. Molyneux. Aust. Chem. Eng. **14**, 13 (1973).
18. C.W. Davies. Ion association. Butterworths, London. 1962. p. 41.
19. J.B. Hasted, D.M. Ritson, and C.H. Collie. J. Chem. Phys. **16**, 1 (1948).
20. J.B. Hasted. Aqueous dielectrics. Chapman and Hall, London. 1973. p. 146, eq. 6.26.
21. B.I. Bleaney and B. Bleaney. Electricity and magnetism. 3rd ed. Oxford University Press, 1976. pp. 44 ff.
22. R. Parsons (Editor). Handbook of electrochemical constants. Butterworths, London. 1959. p. 8.
23. V.E. Bravina. Dokl. Akad. Nauk SSSR, **120**, 815 (1958).
24. F.A. Long and G.C. Nutting. J. Am. Chem. Soc. **64**, 2476 (1942).
25. G. Jones and W.A. Ray. J. Am. Chem. Soc. **59**, 187 (1937).
26. I. Langmuir. Science, **88**, 450 (1938).
27. P.P. Kosakevich. Z. Phys. Chem. (Leipzig), **136**, 195 (1928).
28. C.J. West and C. Hull (Editors). International critical tables. Vol. IV. McGraw-Hill, New York and London. 463 ff (1928); J. Timmermans. Physico-chemical constants of binary systems. Vol. 3. Interscience, New York. 1960. pp. 302 ff.