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# Surface Tension of Electrolytes: Specific Ion Effects Explained by Dispersion Forces

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The surface tension of ionic solutions shows marked specific ion effects not explained by existing theories. The effects are here accounted for by invoking a dispersion force between ions and the air–water interface. The measurements can be explained with reasonable values for the dispersion potential.

## Introduction

Current theories of colloid science do not accommodate “specific ion effects”, that are ubiquitous. Examples are legion: electrolyte activities, bubble–bubble interactions, micelle and microemulsion structure, force measurements, and wettability.<sup>1</sup> The classical Hofmeister series dates from 1888; protein salting out depends on ion-pair, not just salt concentration, as is well-known in biochemistry.<sup>2,3</sup> Recent experiments<sup>4,5</sup> have underlined further the need to go beyond accepted theories. Thus, the cutting efficiency of DNA by enzymes depends strongly on the (supposedly irrelevant) anion of the background salt and of the buffer.<sup>4</sup> Another example is the conformation and solubility of polyelectrolytes. Polyelectrolytes which are insoluble with  $\text{Cl}^-$  as the counterion (e.g., Chitosan) unravel and become soluble with  $\text{CH}_3\text{COO}^-$  present.<sup>1</sup>

Perhaps the simplest specific ion effect occurs at the air–saltwater interface. The surface tension shows a strong dependence on ion pair. Dissolved salts usually increase the surface tension of a water–air interface. The observations are as follows:<sup>6–13</sup> The surface tension increase,  $\Delta\gamma$ , is proportional to the concentration of salt,  $c$ ,  $\Delta\gamma = \Omega c$ , provided the concentration is not too low.  $\Omega$  is usually positive and depends on both the anion and the cation, but usually more strongly on the anions.

The original theory for the change in surface tension was due to Onsager and Samaris.<sup>14</sup> It invokes the repulsive electrostatic image force seen by an ion near an air–water interface. All monovalent ions see the same repulsion. This implies that there is no ion specificity in the theory and all monovalent salts should give the same increment in surface tension. This is in marked disagreement with

the experiments. There have been attempts to improve the Onsager–Samaris theory,<sup>15,16</sup> but these have been incomplete.

It appears that some force specific to each ion needs to be included in a satisfactory theory of the surface tension. Onsager himself recognized this. Here, we propose that it is the dispersion force between the ions and the air–water interface that is the dominant missing effect. Theoretically it can be shown that dispersion energy often dominates the electrostatic image energy.<sup>1</sup> We will show that the dispersion energy alone can have significant effects on the surface tension, which are of the same order of magnitude as those seen experimentally. Dispersion forces provide an obvious candidate for ion specificity, because they depend not merely on the charge but on the excess polarizabilities and electron affinities, which in turn depend on the electronic structure of the ions. Anions (e.g.,  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ) are much more polarizable and have much greater variation in polarizability than do typical cations. This is consistent with the observation that the Hofmeister effect depends markedly on anions.

We first recall the theory of surface tension increment. From this, we derive some results that show that neglected dispersion forces can provide a plausible source of ion specificity. These results are reinforced with numerical computations, that allow us to conclude that inclusion of the neglected dispersion forces may provide the key to other specific ion effects.

## Theory

Consider an aqueous solution of anions (–) and cations (+) each with bulk concentration  $c$  and charge  $\pm e$ , with  $e$  the electron charge. The water is assumed to be a continuum, and for simplicity we consider only 1:1 electrolytes. Each ionic species experiences different forces near the air–water interface. These might be attractive or repulsive, but acting together they lead to an increase or decrease of concentration near the interface. It is this change in concentration that leads to the surface tension increment. Specifically, let the ions be acted upon by external potentials  $U_{\pm}(x)$  as a function of the normal distance  $x$  from the air–water interface to the ion. In general, there will also be a self-consistent electrostatic potential  $\phi$  set up by the ions themselves. These potentials lead via the Boltzmann factor to a usually negative adsorption excess for each species:

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$$\Gamma_{\pm}(c_1) = c_1 \int_0^{\infty} dx \{ \exp(-\beta[U_{\pm}(x) \pm e\phi]) - 1 \} \quad (1)$$

Here,  $\Gamma_{\pm}(c)$  is the number of ions per unit area excluded from the surface, and  $\Gamma_{\pm}(c)/c$  is essentially the length over which they are excluded. Furthermore,  $\beta = 1/k_B T$ , where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. Given  $\Gamma_{\pm}$  as a function of  $c$ , we can calculate the increment in surface tension from the Gibbs adsorption equation as

$$\Delta\gamma(c) = -k_B T \int_0^c dc_1 c_1^{-1} (\Gamma^+(c_1) + \Gamma^-(c_1)) \quad (2)$$

The content of any theory is contained in the potential  $U_{\pm}(x)$  and to a lesser extent in how the electrostatic potential  $\phi$  is calculated.

Onsager and Samaris assumed that the only force acting on the ions is the image force between the ion and the air–water interface. For dissolved ions near the air–water interface, the potential is repulsive and screened:

$$U_{\text{image}}(x) \approx \frac{1}{4\pi\epsilon_w\epsilon_0} \frac{e^2}{4x} \Delta \exp(-2\kappa_D x) \quad (3)$$

where  $\Delta \equiv (\epsilon_w - \epsilon_{\text{air}})/(\epsilon_w + \epsilon_{\text{air}}) \approx 1$ . Here,  $\epsilon_{\text{air}}$  and  $\epsilon_w$  are the dielectric constants of air and water. The inverse Debye length is  $\kappa_D = \sqrt{(2\beta e^2 c_0)/(\epsilon_0 \epsilon_w)}$ . For  $T = 300$  K, this becomes  $\kappa_D = 0.329([c])^{1/2} \text{ \AA}^{-1}$ , where  $[c]$  is the molarity of the salt solution. The image potential is independent of the sign of the charge. This has a drastic simplifying effect in the theory. There is no separation of charges normal to the interface, and hence the electrostatic potential  $\phi$  is zero. The theory thus reduces to the calculation of some integrals, and Onsager and Samaris have no trouble performing these. The resulting limiting law, equivalent to the linear Debye–Hückel theory, does not agree with experiment. Onsager himself noted that other forces must be involved to accommodate specificity but made no attempt to speculate on their nature.

We concentrate on the dispersion forces between the ions and the interface which will be seen to have important and dominating effects on the surface tension. When water molecules with polarizability  $\alpha_w$  are replaced by an ion of polarizability  $\alpha_i$ , the ion will obviously be influenced by dispersion forces. The dispersion potential between an ion and a surface is approximately<sup>1</sup>

$$U_{\text{dispersion}}(x) \approx B/x^3 \quad B \approx (n_w^2 - n_{\text{air}}^2)\alpha^*(0)\hbar\omega_i/8 \quad (4)$$

Here,  $n_w$  ( $n_{\text{air}}$ ) is the refractive index of water (air),  $\hbar\omega_i$  is an electron affinity for the ion, and  $\alpha^*(0)$  is the static excess polarizability of the ion in water. The static excess polarizability is the difference in polarizability of an ion compared to an equivalent volume of water and can be deduced from partial molar volumes of the bulk solutions. The electron affinities are unknown but must be between an infrared and an UV frequency. In Gaussian units,  $\alpha^*$  has dimensions of volume, and a lower bound would be say  $\alpha^* = 1 \text{ \AA}^3 = 10^{-24} \text{ cm}^3$ .  $\alpha^*$  can in fact much larger; for example, for an unhydrated anion of radius  $2 \text{ \AA}$ ,  $\alpha^* \sim 30 \text{ \AA}^3$ .  $\alpha^*$  can be negative because of electrostriction, for instance, in the case of the hydrogen ion,  $\text{H}^+$ , which has no electrons and which is thus less polarizable than water. We can thus estimate the dispersion energy. With the parameters taken to be  $\omega_i = 10^{15} \text{ rad/s}$ ,  $\alpha^* = 2 \text{ \AA}^3$ , and  $n_w = 1.33$ , one find that  $B = 2 \times 10^{-50} \text{ J m}^3$ . Of course,  $B$  depends on several factors and can vary from this value considerably. However, we can regard this as a typical estimate.

We now show that such a dispersion force acting alone can produce surface tension changes close to those seen experimentally. The simplest case occurs when the anion and cation experience exactly the same dispersion interaction, specified by  $B$ , so that there is zero charge density at any point in the solution. In this case, as in the Onsager–Samaris theory, there is no effect due to electrostatics and the surface excess of each species is simply proportional to the concentration. At high concentrations, the image potential becomes screened (at  $1 \text{ M } \kappa_D^{-1} \sim 3 \text{ \AA}$ ) and the dominating contribution comes from dispersion forces. We assume this to be the case and neglect the influence of the image potential. If the  $B$  parameter is positive, the change in surface tension then becomes

$$\Delta\gamma(c) = -2k_B T c \int_0^{\infty} dx \{ \exp(-\beta B x^{-3}) - 1 \} = 2.7 k_B T (\beta B)^{1/3} [c] \quad (5)$$

where  $[c]$  is expressed in moles per liter. Measured values of  $d\Delta\gamma/d[c]$  range from  $0.5 \times 10^{-3}$  to  $1.6 \times 10^{-3} \text{ J m}^3 \text{ mol}^{-1} \text{ L}$ . This implies a range of  $B$  values from  $1.7 \times 10^{-51}$  to  $5 \times 10^{-50} \text{ J m}^3$ . This is certainly within the range of typical values expected for  $B$ . It thus seems that dispersion forces acting alone are sufficient to explain the surface tension increments. Note that the linear dependence in concentration is indeed observed experimentally.

## Numerical Results

The above calculation ignores electrostatics. When the forces acting on the anions and cations are unequal, charge separation results and electrostatics does play a role. In this case, we need to solve a generalized Poisson–Boltzmann differential equation for the self-consistent electrostatic potential  $\phi(x)$ :

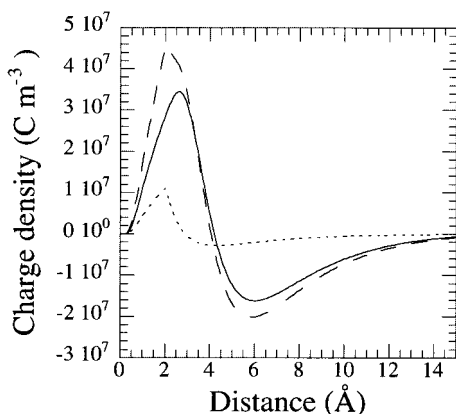
$$\frac{d^2\phi}{dx^2} = -e(c_+ - c_-)/(\epsilon_w\epsilon_0) \quad (6)$$

where the concentrations of the ions are given by

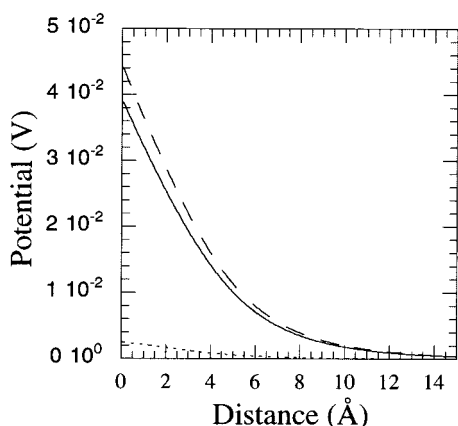
$$c_{\pm} = c_0 \exp(-\beta(\pm e\phi + U_{\text{image}} + B_{\pm}/x^3)) \quad (7)$$

In general, this equation must be solved numerically. In practice, this is not trivial because of numerical instabilities. The numerical method that we have used is as follows. We first solve the equation on some finite interval  $L$ , which is much larger than any other length scale in the problem. Assume boundary conditions  $\phi(L) = 0$  and  $\phi(0) = \phi_0$ , where  $\phi_0$  is an estimate of the actual surface potential. The Poisson–Boltzmann equation is then solved using the method of relaxation, repeatedly adjusting  $\phi_0$  until the net charge density in the system approached zero. This last step is crucial, because any finite charge in the system would create a long-range electric field which would attract charges from infinity.

Before we go on to calculate the derivative of the surface tension with respect to molar concentration, we will first consider the charge distribution. A mathematical consequence of overall charge neutrality is that the surface excesses for the two different species are equal. However, this does not mean that the different species have the same spatial distribution. The cations, that may have negative excess polarizability and certainly a smaller polarizability than the anions, accumulate closer to the surface. This leads to the charge distributions shown in Figure 1 where we have used a cutoff radius of  $2 \text{ \AA}$ . Figure 2 is a plot of the corresponding potential. One should



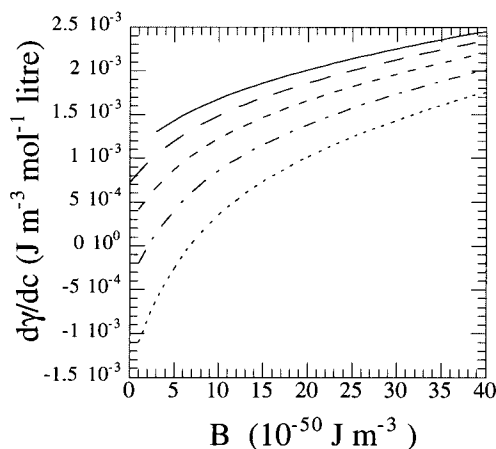
**Figure 1.** The charge distribution in a 1 M electrolyte for three different combinations of dispersion constants. The combinations are (in units of  $10^{-50} \text{ J m}^3$ ) 0, -1 (dotted line), 31, 0 (solid line), and 31, -2 (dashed line). The cutoff radii were taken to be 2 Å.



**Figure 2.** The self-consistent potential corresponding to the charge distributions shown in Figure 1. The combinations are (in units of  $10^{-50} \text{ J m}^3$ ) 0, -1 (dotted line), 31, 0 (solid line), and 31, -2 (dashed line). The cutoff radii were taken to be 2 Å.

observe that the magnitude of the potentials at the interface is reasonable. Surface potential differences, due to added salts, measured in experiments are usually positive.<sup>17</sup> Our calculated surface potentials in the absence of any measurements are negative, but it is not clear if these can be compared directly with the experimental surface potentials.

The numerically evaluated values of  $d\gamma/dc$  versus  $B_-$ , at a concentration of 1 M, are shown in Figure 3 for different values of  $B_+$ . These values are similar in range to those seen in the experiments shown in Table 1. As can be seen, these vary from  $0.76 \times 10^{-3} \text{ J m}^3 \text{ mol}^{-1} \text{ L}$  for  $\text{CH}_3\text{COOK}$  to  $2.1 \times 10^{-3} \text{ J m}^3 \text{ mol}^{-1} \text{ L}$  for  $\text{NaCl}$ . Measuring surface tensions is a difficult task, and there are large experimental inaccuracies in the values given in the table. If one compares the values given by different authors and at different times, the spread in values is very large. We have used mainly the values given by Weissenborn and Pugh, if only for illustrative purposes. Bearing these limitations in mind, a very simple procedure to deduce values for the dispersion constants might be as follows. Systematically guess at different values for  $B_{\text{Na}}$  where each value produces one unique value for each of the three anions. With these values, we find three different values for  $B_{\text{K}}$ . Of course, these three values should in principle be the same. However, because of the great uncertainty



**Figure 3.**  $d\gamma/dc$  in a 1 M electrolyte as a function of the anion dispersion constant ( $B_-$ ). Counted from above in the figure, the different curves correspond to  $B_+ = 3, 0, -3, -6, -9 \times 10^{-50} \text{ J m}^3$ .

**Table 1.** Experimental Values of  $d(\Delta\gamma)/dc$  for 10 Different Electrolytes as Measured by Different Groups<sup>a</sup>

electrolyte	Weissenborn <sup>b</sup> /literature <sup>b</sup> /Aveyard <sup>c</sup>	theory
NaCl	2.08/1.55/1.70, 1.75	2.10
NaBr	1.83/1.97/-	1.83
NaI	1.23/1.45, 1.21/-	1.24
KCl	1.85/1.60, 1.65/1.59, 1.65	1.90
KBr	-/-/1.36	1.43
KI	-/-/1.24, 1.16	0.91
$\text{CH}_3\text{COONa}$	0.93/0.54/-	1.1
$\text{CH}_3\text{COOK}$	0.76/0.45/-	0.58
$\text{CH}_3\text{COOLi}$	0.84/-/-	0.87
LiCl	1.98/1.63/-	1.99

<sup>a</sup> The values are given in SI units [ $10^{-3} \text{ J m}^3 \text{ mol}^{-1} \text{ L}$ ]. The theoretical values at 1 M are given in the last column. The  $B$  constants used to obtain these values were -1, -3, -5, 31, 21, 7, and 5 (in units of  $10^{-50} \text{ J m}^3$ ) for  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{CH}_3\text{COO}^-$ , respectively. <sup>b</sup> Reference 6. <sup>c</sup> Reference 8.

in the experimental values, getting a perfect match is a difficult, and perhaps not even possible, task. Using an average value for  $B_{\text{K}}$ , we can evaluate  $d\gamma/dc$  for the three potassium salts. This procedure should be repeated until a good fit has been achieved. Only after this procedure was finished, we added the last four salts given in Table 1. This provided a simple test of the validity of the present approach. We used the previously determined dispersion potentials for sodium and potassium together with reasonable values for lithium and acetate. As can be seen in Table 1, a reasonably good fit was found for these salts too.

One should observe that the surface tension increment for the combination  $B_- = 12 \times 10^{-50} \text{ J m}^3$  and  $B_+ = -5 \times 10^{-50} \text{ J m}^3$  is very close to the result for  $B_- = 10 \times 10^{-50} \text{ J m}^3$  and  $B_+ = -4 \times 10^{-50} \text{ J m}^3$ . This means that the result at high concentrations to some extent is additive for the different dispersion contributions. It is thus not a straightforward task to find a unique set of dispersion coefficients. We are not saying that the results given in Table 1 are "the correct"  $B$  constants to be used. There will also be substantial influences from the way dispersion forces are handled in the surface region. We have furthermore not taken into account that the ions have different ion sizes. Despite this, it is certainly possible to fit the data using reasonable values of the dispersion constants.

### Summary and Conclusions

We have shown, by direct calculation and comparison with experiments, that one way of accounting for specific

ion effects in simple electrolyte solutions is via inclusion of short-range dispersion forces. Certainly, at high salt concentrations above say 0.1 M they dominate the electrostatic image potential. What we have shown is that dispersion forces have an important effect, but it would be wrong to claim that they give the full story. Other forces, particularly those involving water structure, may play a role. For instance, recent work by Marrinck and Marcelja<sup>18</sup> has highlighted the diffuse nature of the air–water interface. This implies that as the ion comes up to the interface it experiences a repulsion due to the decrease in dielectric constant. Our view however is that it is important to first include the dispersion forces which we can estimate simply, before attempting to tackle this or more complicated charged interface problems, by more sophisticated electrostatic theories of statistical mechanics.

One referee has remarked that the general consensus is that anions approach the air/water interface more closely than cations, as a result of hydration effects, and thus the surface potentials have opposite sign to those predicted by us. We have of course not taken hydration effects fully into account in this study, because we have limited ourselves to what can be calculated with some certainty. However, we believe that the question of surface potentials is one which is very subtle. In an experimental measurement of surface potential, one must have two electrodes.

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These of course perturb the interface, and double layers will form around each electrode. This does not happen in our system, because we can “measure” the potential difference between the surface and the bulk without introducing any electrodes. To calculate the actual potential difference between two electrodes, we would need to calculate the effect of the electrodes upon the ions, including any dispersion and image forces, and this is certainly a more complicated problem than we have solved here. If we could measure the potential predicted in our theory, this would indeed be very useful, because it would yield an extra piece of information for calculating the dispersion constants.

Two further remarks should be made in conclusion. (1) For the water–oil interface, one often has positive adsorption,<sup>8</sup> for example, for KI, whereas this ion adsorbs negatively at the air–water interface. Such effects are clearly accommodated by dispersion effects; cf. eq 4, where  $n_{\text{air}}$  is replaced by  $n_{\text{oil}}$ , that is, effectively accommodating a change of sign of the potential. (2) For air–water and corresponding systems, interactions are dominated by the temperature-dependent part of the Lifshitz theory. This is<sup>1</sup> exactly equivalent to the extension of the linear form of the Onsager theory to two interfaces. Hence, conventional theories of interactions ignore ion specificity and are as inadequate as Onsager limiting laws.

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