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## XVI

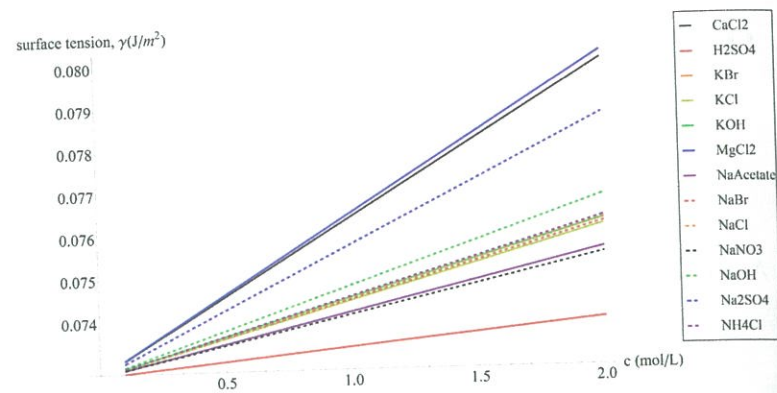
### On the surface tension of electrolyte solutions

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The surface tensions of aqueous electrolyte solutions in general increase linearly with concentration over a wide range of concentration. Here we analyse this data using the Gibbs Adsorption Isotherm to evaluate the concentration of electrolytes in the surface layer and derive a simple expression whereby the concentration in the surface layer can easily be calculated.

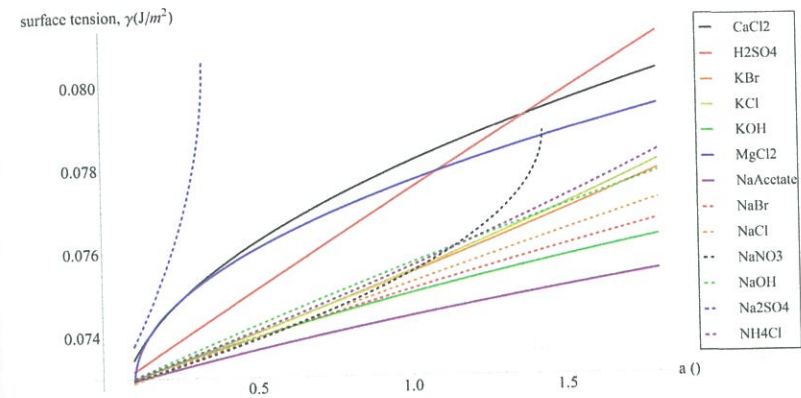
Specific ion effects are manifest in all manner of measurements from the stability of proteins as originally investigated by Hofmeister<sup>1</sup> to the combining rules that govern the inhibition of bubble coalescence.<sup>2,3</sup> Here we wish to discuss a particular specific ion effect that is well known and appears at first glance to be very simple. If the surface tension of aqueous salt solutions are measured, a plot of surface tension versus concentration reveals a straight line over a wide concentration range (see Figure XVI.1).<sup>4</sup> Therefore the data can be described by the surface tension gradient  $dy/dC$ , which is constant and positive indicating that the electrolyte ions are depleted from the interface. The same linear correlation between surface tension and concentration is found for other electrolytes with only a few exceptions.<sup>4-6</sup> The magnitude of the gradient varies but remains positive for most electrolytes other than acids. The surface tension is of particular interest because it reflects the interfacial



**Figure XVI.1.** Surface tension versus concentration for a range of electrolytes in water. Using slopes determined from experimental data.

concentration of ions, which is thought to be a significant contributor to the many observed specific ion effects. In the past decade surface sensitive spectroscopic techniques have provided a direct measure for investigating the surface propensity of individual ions,<sup>7,8</sup> however the data obtained by these techniques and advanced simulation methods have not been resolved with surface tension measurements. Resolution is not expected to be immediate or straightforward as the techniques may well probe a different surface depth, only some ions are revealed spectroscopically, the effect of individual ions cannot be measured by surface tension measurements and it is expected that the concentration profile of the ions in the interface is complex, being oscillatory.<sup>9</sup> We wish to investigate the form of the surface tension data in some more detail and attempt to quantitatively analyse the data using the Gibbs Adsorption Isotherm.

As surface tension is a thermodynamic quantity defined as the change in Gibbs Free Energy with area, one would expect that the concentration is best expressed as activity rather than molarity. The activity coefficient varies considerably from unity for electrolytes



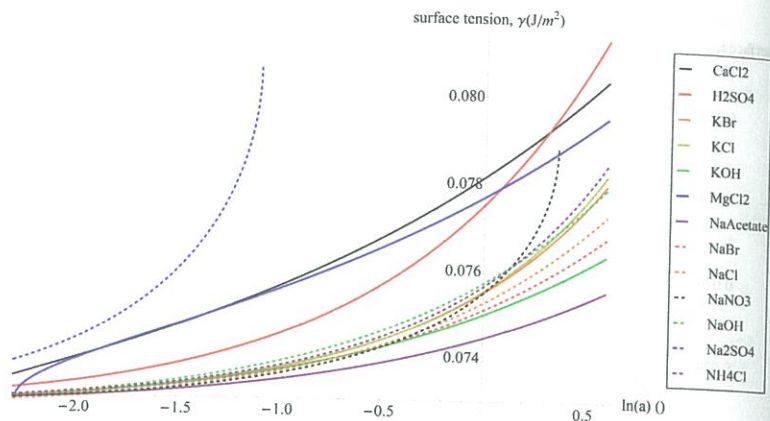
**Figure XVI.2.** Surface tension of aqueous electrolyte solutions as a function of the activity of solution.

and changes as a function of salt concentration. Therefore, one might expect that a plot of surface tension versus activity will not exhibit the linearity seen in plots of surface tension versus concentration. In Figure XVI.2 we have plotted the relationship between concentration and activity for a range of electrolytes. Within the accuracy of experimental measurements the relationship is linear for many of the electrolytes but not for all. What is not clear is why there should be a linear correlation. With reference to the Gibbs Adsorption Isotherm, the surface excess of electrolyte  $\Gamma$  can be calculated from the surface tension  $\gamma$  and the activity  $a$ , where  $R$  is the gas constant and  $T$  the temperature in Kelvin.

$$\Gamma_{\text{electrolyte}} = \frac{-1}{RT} \times \frac{d\gamma}{d \ln a} \quad (1)$$

Note the surface excess is a relative concentration, that is, it is the concentration in the surface layer relative to the bulk. What is clear is that  $\Gamma$  is proportional to  $-d\gamma / d \ln a$ . As the surface tension increases with activity (and concentration) the surface layer is depleted with respect to the bulk by the magnitude of  $\Gamma$ . If the data is plotted as





**Figure XVI.3.** Surface Tension versus the natural logarithm of the activity for aqueous electrolyte solutions. Within the paradigm of the Gibbs Adsorption Isotherm the slope of this plot is proportional to the surface excess.

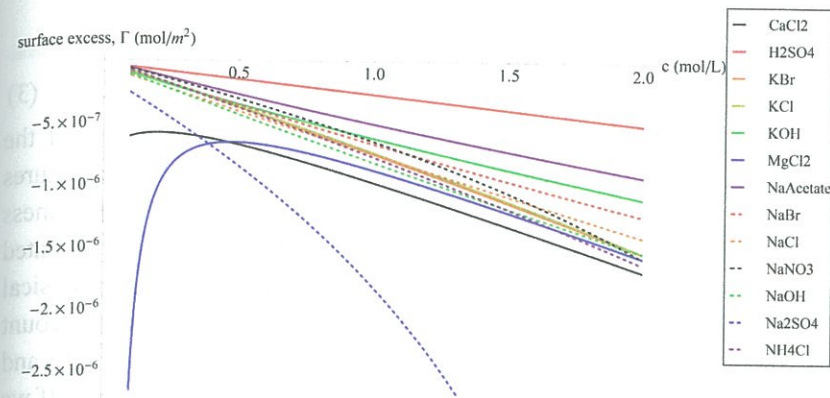
surface tension versus the natural logarithm of the activity as in Figure XVI.3, the surface excess can be calculated using equation 1, where the  $d\gamma/d\ln a$  term is the slope of the plot at a particular value of the activity.

Noting that the surface tension changes linearly with activity we can write  $d\gamma/d\ln a = ma$ , where  $\frac{d\gamma}{da} = m$

combining with equation (1) we obtain a simple expression for the surface excess.

$$\Gamma_{\text{electrolyte}} = \frac{-ma}{RT} \quad (2)$$

If  $R$  is expressed in  $\text{J mol}^{-1} \text{K}^{-1}$  then  $\Gamma$  is in units of  $\text{mol m}^{-2}$  and is therefore a surface layer concentration, that is a two dimensional concentration. In Figure XVI.4 we present the surface excess (two dimensional concentration) for electrolytes as a function of the bulk concentration. The Gibbs Adsorption isotherm chooses a particular dividing plane such that the surface excess of water is zero. It is



**Figure XVI.4.** Surface Excess ( $\Gamma$ ) of electrolytes versus bulk concentration calculated using the Gibbs Adsorption isotherm. The negative sign indicates that the surface is depleted of electrolyte.

unclear exactly where this dividing plane is located with respect to the interface. However, it is generally accepted that the interfacial depth is  $\sim 1$  nm therefore by assuming a depth of the interface the surface excess can be converted to a three dimensional concentration. Moreover, if the slope of  $d\gamma/d\ln a$  is positive, the surface excess will be negative. That is the concentration of electrolyte in the surface layer will in most instances be less than that in bulk, as is commonly understood. As such the actual concentration of the surface phase can be determined from the bulk concentration minus the surface excess when it is expressed as a 3D concentration. This concentration is of interest, as it will reflect the degree to which the surface layer is depleted of electrolyte.

As the depth of the interface is not actually known we have performed this calculation with a series of interfacial depths in an effort to discern the surface excess expressed as a three dimensional concentration. This enables the actual concentration of electrolyte in the surface layer to be determined.



The expression for this is

$$\Psi_{\text{electrolyte}} = c + \frac{ma}{RTl} \quad (3)$$

Where  $c$  is the bulk concentration and  $l$  is the thickness of the surface phase and will be less than 4 nm. This data is shown in Figures XVI.5, 6, 7. What is apparent is that for a surface layer of thickness 6Å, the thinnest layer that is suggested in the literature,<sup>10</sup> the calculated concentration of NaCl in the surface layer is negative. This is unphysical and implies that the surface layer thickness must be greater to account for the large depletion of NaCl in the surface. Surface layers of 8Å and above give positive concentrations of NaCl in the surface layer. If we make the assumption that the surface layer is the same for different types of electrolyte it is likely that the surface layer thickness has to be set to a value > 18Å to accommodate electrolytes that more strongly effect the surface tension, such as MgCl<sub>2</sub>.

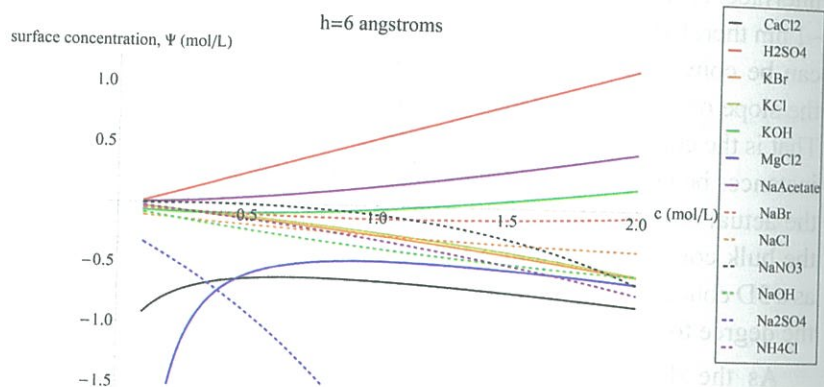


Figure XVI.5. Surface excess expressed as Molarity under the assumption that the surface layer is 6 Ångstroms thick versus the bulk concentration. Note that the surface concentration is determined by the sum of the bulk concentration and the surface excess (which is negative).

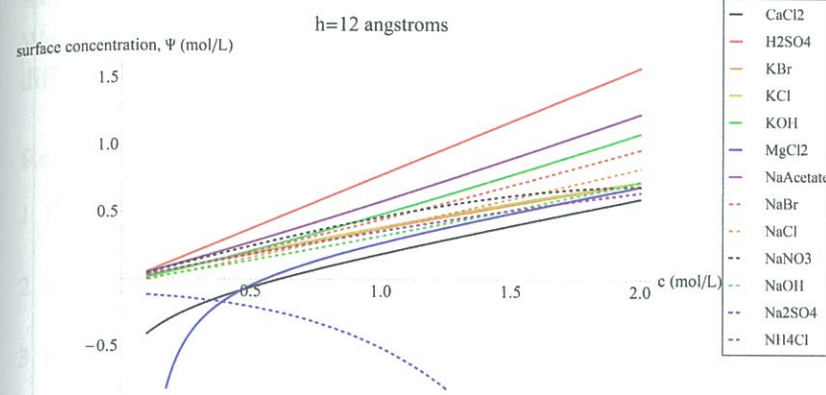


Figure XVI.6. Surface excess expressed as Molarity under the assumption that the surface layer is 12 Ångstroms thick versus the bulk concentration. Note that the surface concentration is determined by the sum of the bulk concentration and the surface excess (which is negative).

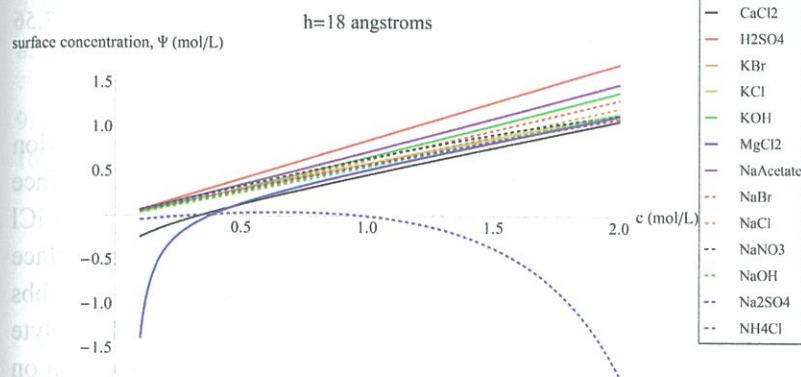
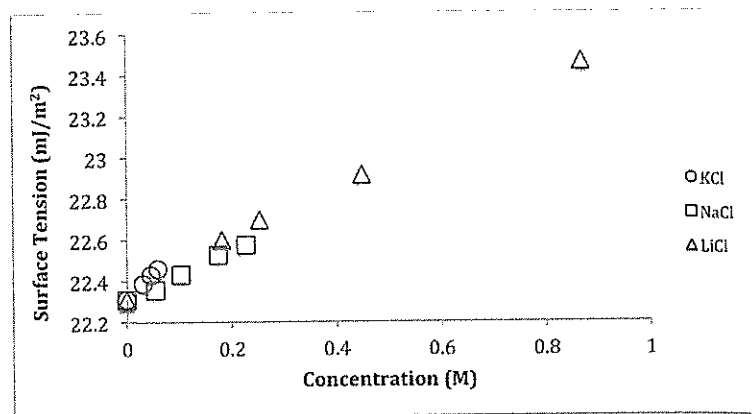


Figure XVI.7. Surface excess expressed as Molarity under the assumption that the surface layer is 18 Ångstroms thick versus the bulk concentration. Note that the surface concentration is determined by the sum of the bulk concentration and the surface excess (which is negative).

We have recently investigated the effect of electrolytes on the surface tension of non-aqueous electrolytes. The resulting data is very



**Figure XVI.8.** Surface tension of electrolytes measured in methanol solutions as a function of concentration. Within the uncertainty in the measurements there is a linear correlation between surface tension and concentration for each electrolyte. The magnitude of the gradient is similar to what is measured for electrolytes in aqueous solution. The magnitude of the gradient in surface tension is  $1.21 \times 10^{-3} \text{ J m}^{-2} / \text{M}$  for NaCl,  $1.30 \times 10^{-3} \text{ J m}^{-2} / \text{M}$  for LiCl and  $2.56 \times 10^{-3} \text{ J m}^{-2} / \text{M}$  for KCl.

similar in form to that of aqueous solutions in that the surface tension increases with electrolyte concentration and within error the surface tension versus concentration is linear. Data for NaCl, KCl and LiCl in methanol obtained using a KSV Cam 100 pendant drop surface tensiometer are presented in Figure XVI.8. Analysis using the Gibbs Adsorption isotherm could be conducted as above for electrolyte solutions, but we do not currently have the necessary information on the activity coefficients of electrolytes in these solutions. Regardless, the data suggests that the surface excess behaves in a similar manner to aqueous solutions, highlighting that the overall behaviour is determined primarily by the electrolyte, with the solvent playing a minor role.

### Acknowledgments

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