Surface tension of strong electrolytes

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Abstract. – We present a theory which accounts for the increase in interfacial tension of water due to the presence of 1:1 electrolyte. The agreement between the theory and experiment is excellent, extending all the way to relatively high salt concentrations of 1 M. For low concentrations of electrolyte the theory reduces to the Onsager-Samaras limiting law.

Contrary to surfactant solutions, aqueous electrolytes possess surface tensions higher than pure water. An explanation of this curious phenomenon has been advanced by Wagner [1] based on then recently introduced Debye-Hückel theory of strong electrolytes [2]. This work was further extended by Onsager and Samaras (OS) [3], who were able to derive a limiting law for surface tension similar to the one obtained by Debye and Hückel for bulk properties of electrolyte solutions. The OS limiting law is universal in the sense that it does not depend on specifics of electrolyte [4–7]. For low concentrations, good agreement has been found between the OS theory and the experiments [5,6]. However, at larger concentrations the OS theory strongly underestimates the value of surface tension as compared to experiments [8].

Since the original work of Wagner and OS, the route to surface tension has relied on the Gibbs adsorption isotherm [9,10]. This equation relates the derivative of surface tension with respect to chemical potential to the number of ions adsorbed into the interfacial region [8, 11, 12]. The calculation is intrinsically grand canonical, since the interface is thought to be in contact with a reservoir of solute, *i.e.* bulk electrolyte. It has been argued, however, that a canonical calculation, besides being conceptually simpler, might actually lead to better results as it relies on fewer approximations [13]. Within the canonical formalism the Helmholtz free energy is directly related to the surface tension, bypassing use of the Gibbs adsorption isotherm.

To see how this work, consider a neutral electrolyte solution of $N_t = N_+ + N_-$ ions and N_s solvent molecules confined to a cylinder of height H and a cross-sectional area A. The interface can be idealized as the Gibbs dividing surface for which the surface excess of solvent is zero [14]. At *fixed volume and temperature*, the differential Helmholtz free energy is $dF = \sigma\, dA + \mu_t\, dN_t + \mu_s\, dN_s$, where σ is the surface tension and μ_t and μ_s are the solute
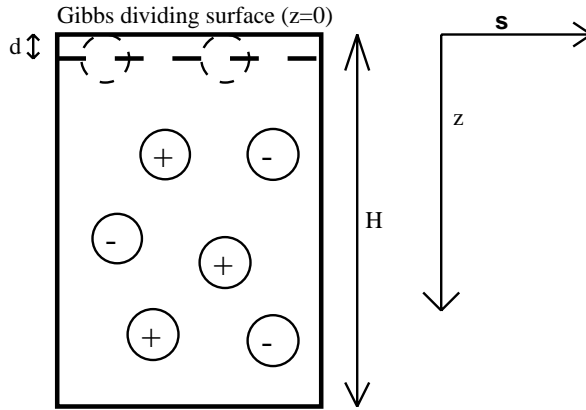
Fig. 1 – Electrolyte solution with liquid and vapor separated by the Gibbs dividing surface. The dielectric constant of vapor is ϵ_0 and that of electrolyte is ϵ. The hydration of ions prevents their centers from coming closer than $d = a/2$ to the Gibbs dividing surface.

and the solvent chemical potentials, respectively. Canonically, the number of solute and solvent particles is fixed. Euler's theorem for first-order homogeneous functions then allows to integrate the above equation leading to the expression for the excess surface tension over that of pure solvent,

$$\sigma^{\text{ex}} = \lim_{A \to \infty} \frac{1}{A} \lim_{H \to \infty} \left(F - F^{\text{bulk}} \right). \tag{1}$$

The bulk free energy can be obtained by imposing periodic boundary conditions before taking the thermodynamic limit. Thus, within the canonical formalism the excess surface tension is equivalent to the Helmholtz free energy per unit area necessary to create an interface.

To perform calculations we shall resort to restricted primitive model (RPM) of electrolyte. Within this approach, N_{t} ions are treated as hard spheres of diameter a and charge $\pm|q|$ located at the center. The solvent and vapor are modeled as uniform mediums of dielectric constant ϵ and ϵ_0, respectively. We shall take the Gibbs dividing surface [14] as the interface between liquid and vapor. In aqueous solutions, ions are surrounded by water molecules so that a is the diameter of a hydrated ion. Polarization of surrounding solvent and the corresponding decrease of free energy are responsible for electrolyte's good solubility in water. To leave the aqueous environment, an ion has to shed its hydration sphere, which requires high cost in free energy. Therefore, very few ions will be present in the vapor phase. Furthermore, hydration prevents the centers of ions from coming closer than $d = a/2$ to the Gibbs dividing surface [8, 11], see fig. 1.

The bulk free energy of electrolyte can be calculated straightforwardly by imposing periodic boundary conditions in fig. 1, and then taking the thermodynamic limit. Note that with periodic boundary conditions there is no interface and no ion free layer. Application of Debye-Hückel theory [2] leads directly to the classic result

$$F^{\text{bulk}} = k_{\text{B}} T N_{\text{t}} \left[\ln \left(c_{\text{b}} \Lambda^3 \right) - 1 \right] - \frac{q^2 \kappa}{3\epsilon} N_{\text{t}}, \tag{2}$$

where Λ is the de Broglie thermal wavelength, $c_{\text{b}} = N_{\text{t}}/2AH$ is the bulk concentration of electrolyte, and $\kappa = \sqrt{8\pi q^2 c_{\text{b}}/\epsilon k_{\text{B}} T}$ is the inverse Debye length. The first term is the entropic mixing contribution, while the second term is due to electrostatic interactions between the

particles. It is important to note that in the bulk the mean electrostatic potential is zero, so that the electrostatic contribution to the free energy is purely correlational.

To simplify the calculations we have taken a point particle limit. This is quite reasonable if the concentration of electrolyte is low. However, we expect that for canonical calculation of surface tension the limit $a \to 0$ should provide a reasonable approximation even at moderate densities, if the ion-free layer of width $d = a/2$ is taken into account. The reason for this is that in eq. (1) enters only the difference between the total free energy and the bulk free energy. Thus, the contributions to surface tension arising from the hard cores of solute particles — away from the ion-free layer— should mostly cancel out.

In the presence of an interface the system becomes inhomogeneous. The total free energy can still, however, be subdivided into that due to an ideal entropy of mixing and an electrostatic contribution [15],

$$F = k_{\mathrm{B}} T N_{\mathrm{t}} \big[\ln \left(c \Lambda^3 \right) - 1 \big] + F^{\mathrm{el}}, \tag{3}$$

where because of an ion-free layer the concentration now is $c = N_{\mathrm{t}}/2A(H - d)$.

The electrostatic contribution to the total free energy can be calculated in the spirit of Debye-Hückel theory. Let us fix an ion some distance z_c from the interface. What is the potential that this ion feels? Clearly there are two contributions, one arising from the induced charge due to dielectric discontinuity across the Gibbs dividing surface, and another due to polarization of ionic atmosphere. Inside the electrolyte, the electrostatic potential satisfies the linearized Poisson-Boltzmann equation

$$\nabla^2 \varphi - \kappa^2 \varphi = -\frac{4\pi q}{\epsilon} \delta(z - z_c), \tag{4}$$

where to simplify the calculations we have fixed the inverse screening length at its bulk value $(z \to \infty)$. Inside the ion-free layer and in the vapor phase no free charges are present, and the electrostatic potential satisfies the Laplace equation, $\nabla^2 \varphi = 0$. The boundary condition is the continuity of electrostatic potential and the displacement field across the Gibbs dividing surface, and across the interface separating electrolyte from the ion-free layer. Since the dielectric constant of vapor is so much smaller than that of water, $\epsilon/\epsilon_0 \approx 80$, it is reasonable to set it equal to zero, $\epsilon_0 = 0$.

To solve eq. (4) it is convenient to set up a cylindrical coordinate system [16, 17] $(z, \boldsymbol{s})$, see fig. 1. Fourier transforming in the $\boldsymbol{s}$-direction and taking the limits $A \to \infty$ and $H \to \infty$, eq. (4) can be integrated to yield, for $z \geq d$,

$$\varphi(s, z) = \frac{1}{2\pi} \int_0^\infty k \, \mathrm{d}k J_0(ks) \tilde{\varphi}(k, z), \tag{5}$$

where $J_0(x)$ is the Bessel function of order zero, and

$$\tilde{\varphi}(k, z) = \frac{2\pi q}{\epsilon p} \left\{ e^{-p|z - z_c|} + e^{-p(z + z_c - 2d)} \frac{p \cosh(kd) - k \sinh(kd)}{p \cosh(kd) + k \sinh(kd)} \right\}, \tag{6}$$

with $p = \sqrt{k^2 + \kappa^2}$. Substituting eq. (6) into eq. (5) yields the expression for electrostatic potential in the region $z \geq d$. The potential felt by the fixed ion can be obtained by taking the limit $z \to z_c$ and $s \to 0$ in eq. (5),

$$\psi(z_c) = -\frac{q\kappa}{\epsilon} + \frac{q}{\epsilon} \int_0^\infty \mathrm{d}k e^{-2k(z_c - d)} \frac{k \big[p \cosh(kd) - k \sinh(kd) \big]}{p \big[p \cosh(kd) + k \sinh(kd) \big]}. \tag{7}$$

The first term of eq. (7) is the electrostatic potential resulting from ionic atmosphere. The integral is due to the existence of the liquid-vapor interface. The adsorption potential, *i.e.* the work necessary to bring an ion from bulk to some distance z from the interface, can be obtained from eq. (7) using the Güntelberg charging process [18], in which the ion is charged from zero to its full charge q,

$$W(z) = \frac{q^2}{2\epsilon} \int_0^\infty \mathrm{d}k e^{-2k(z-d)} \frac{k\left[p\cosh(kd) - k\sinh(kd)\right]}{p\left[p\cosh(kd) + k\sinh(kd)\right]}. \tag{8}$$

The adsorption potential induces an inhomogeneity in the ionic density given by the *normalized* Boltzmann distribution,

$$\rho_\pm(z) = \frac{N_\pm e^{-\beta W(z)}}{A \int_d^H e^{-\beta W(z)}\,\mathrm{d}z}. \tag{9}$$

The electrostatic energy is

$$E = \frac{A|q|}{2} \int_d^H \left[\rho_+(z) + \rho_-(z)\right]|\psi(z)|\mathrm{d}z, \tag{10}$$

which in the limit $H \to \infty$ reduces to

$$E = -\frac{q^2\kappa}{2\epsilon}N_\mathrm{t} + 2Ac \int_d^\infty e^{-\beta W(z)} W(z)\,\mathrm{d}z. \tag{11}$$

The electrostatic *free energy* can now be obtained using the Debye charging process in which all the particles are charged simultaneously from zero to their full charge [2, 15, 19],

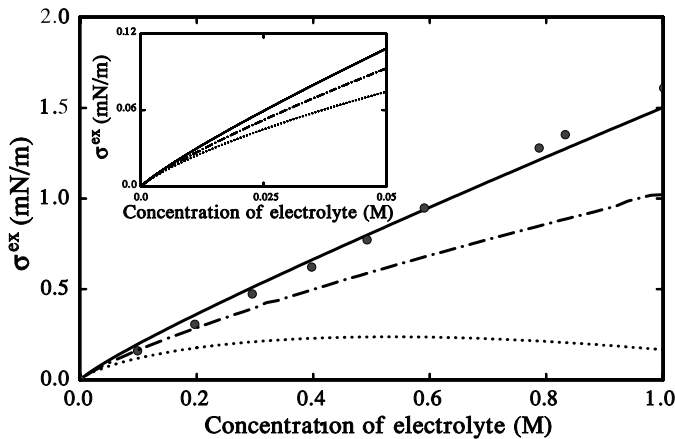$$F^\mathrm{el} = 2 \int_0^1 E(\lambda q)\frac{\mathrm{d}\lambda}{\lambda}. \tag{12}$$

Fig. 2 – The solid curve is the excess surface tension given by eq. (13). The dashed curve is the surface tension in the point particle limit, $d = 0$. The dotted curve is the Onsager-Samaras limiting law. Circles are the experimental data for NaCl from ref. [20]. Inset shows that, for very low concentrations, eq. (13) approaches the OS limiting law.
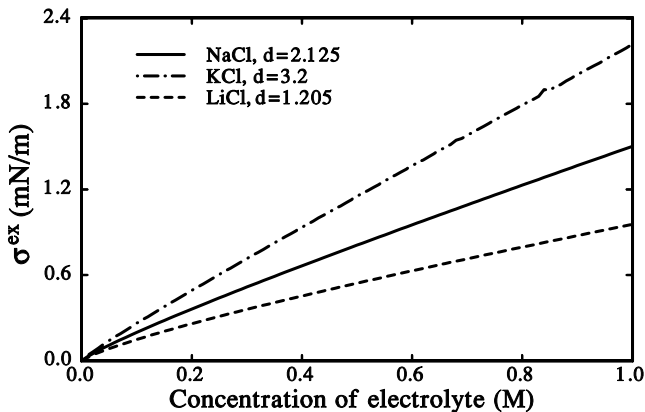
Fig. 3 – Surface tension as a function of concentration for three monovalent electrolytes.

Substituting eq. (2) and eq. (3) into eq. (1) yields the expression for excess surface tension,

$$\sigma^{ex} = 2k_{\mathrm{B}}Tcd + \sigma_0^{\mathrm{ex}} I\left(\frac{d}{b}, \kappa b\right), \tag{13}$$

where $\sigma_0^{\mathrm{ex}} = q^2 c/2\epsilon$ and $b = q^2/2\epsilon k_{\mathrm{B}}T$ is half the Bjerrum length. For water at room temperature $b \approx 3.6\,\text{Å}$. The scaling function $I(x, y)$ follows directly from eqs. (11) and (12).

The first term of eq. (13) is the result of decrease in entropy of mixing, compared to that of bulk electrolyte, due to the ion-free layer. The second term is purely electrostatic, arising from the dielectric discontinuity across the liquid-vapor interface and the positional correlations between the ions of electrolyte. Although the dielectric constant of water varies continuously across the interface, we have approximated it by a step function, discontinuous across the Gibbs dividing surface. For water at room temperature $\epsilon = 78.54$. In fig. 2 we plot the excess surface tension due to NaCl, $a = 4.25\,\text{Å}$. Excellent agreement is found between theory and experiment, extending all the way to 1 M concentrations of electrolyte.

In fig. 3 we present a plot of surface tension for two other aqueous monovalent electrolytes at room temperature, KCl and LiCl. It is evident that the excess surface tension is an increasing function of the hydration diameter. Unfortunately, no experimental data was available to us to compare the theory with experiment for these electrolytes.

A simple theory which accounts for the increase in surface tension of water due to 1:1 electrolyte is presented. Unlike the original Onsager-Samaras grand-canonical calculation based on the Gibbs adsorption isotherm, our method is intrinsically canonical. This provides a clearer understanding of the approximations necessary in order to make the calculations tractable. Thus, we show that hydration of ions leads to formation of an ion-free layer which increases the excess surface tension by as much as 50% for high concentrations of electrolyte.

Good agreement between theory and experiment —extending all the way to fairly high salt concentrations up to 1 M, *without any adjustable parameters*— suggests that the theory captures the main physical effects responsible for the observed phenomenon. For very low concentrations of salt, the excess surface tension approaches the Onsager-Samaras limiting law $\sigma_l^{\mathrm{ex}} = \sigma_0^{\mathrm{ex}}[-\ln(\kappa b) - 2\gamma_{\mathrm{E}} + 3/2]$, where $\gamma_E = 0.577215665\ldots$ is Euler's constant.

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