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SHORT COMMUNICATION

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Surface tension of electrolyte solutions

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Abstract A simple analytic expression is derived for the excess surface tension of electrolyte solutions, which is in good agreement with the experimental data on NaCl in the concentration range up to as high as 1 M. This expression is consistent with the following two theories: (i) The recent theory of Levin and Flores-Mena (Europhys Lett (2001) 56:187), who demonstrated the important contribution of the formation of an ion free layer at the air–electrolyte solution interface, and (ii) the Onsager–Samaras theory (J Chem Phys (1934) 2:528) modified by taking into account the ion-free layer effect. It is shown that the excess surface tension consists of three parts: the contributions of the ion-free layer, the image interaction between the electrolyte ions and the ion-free layer, and the image interaction between the electrolyte ions and air.

Keywords Surface tension · Electrolyte · Ion-free layer

Introduction

The surface tension of an electrolyte solution in contact with air is larger than that of pure water. The excess surface tension has been considered to be caused by the electrostatic image repulsive interaction between electrolyte ions and air so that the electrolyte ions are repelled from the air–water interface (negative adsorption of electrolyte ions at the air–water interface). This explanation, which was first proposed by Wagner [1] and later was further extended by Onsager and Samaras [2], has been generally accepted for a long time. Quite recently, however, Levin and Flores-Mena [3] and Levin [4, 5] have pointed out two important problems involved in the Onsager and Samaras theory. First, Levin and Flores-Mena [3] showed that the Onsager–Samaras theory [1] did not take into account the contribution of the formation of an ion-free layer at the air–solution interface due to the hydration of electrolyte ions, which becomes appreciable as the electrolyte concentration increases. The inclusion of the presence of an ion-free layer explains well the nearly linear dependence of the excess surface tension of electrolyte solutions upon the electrolyte concentration observed experimentally [6]. The second problem is concerned with the Gibbs adsorption isotherm. As pointed out by Levin and Flores-Mena [3] and Levin [4, 5], the Onsager–Samaras theory [2], which employs the integration of the Gibbs adsorption isotherm, is based on a grand canonical approach. The theory of Levin and Flores-Mena [3], on the other hand, is derived directly from the Helmholtz free energy of the air–solution interface without recourse to the Gibbs adsorption isotherm. This theory is thus based on a canonical approach. If the ion-free layer effects are incorporated into the Onsager–Samaras theory, then in the thermodynamic limit, both approaches should give identical results. Actually, however, both theories give different results because of approximations involved in the respective theories.

In the present paper, we derive a simple analytic expression for the surface tension of electrolyte solutions that is consistent with both canonical and grand canonical approaches and show that the excess surface tension is composed of the contributions of an ion-free layer, the image interaction between the electrolyte ions and the ion-free layer, and the image interaction between ions and air.

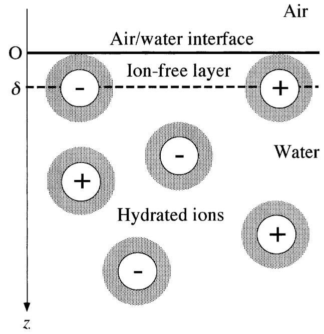

Fig. 1 The model of Levin and Flores-Mena [3] for the interface between an electrolyte solution and air at $z = 0$. Hydration of ions prevents their centers from coming closer than δ (δ = radius of an hydrates ion) to the air–solution interface, forming an ion-free layer of thickness δ

Surface tension of an electrolyte solution

Consider the surface tension γ of a symmetrical electrolyte solution of bulk concentration (number density) n and valence v in contact with air. We take a z-axis perpendicular to the planar air–water interface with its origin $z = 0$ at the Gibbs dividing surface so that the region $z < 0$ corresponds to air and $z > 0$ to the solution phase, as shown in Fig. 1. Following Levin and Flores-Mena [3], we first modify the original Onsager–Samaras theory [2] (which is based on the integration of the Gibbs adsorption isotherm) by taking into account the presence of an ion-free layer. We start with the Gibbs adsorption isotherm:

$$d\gamma = -kT\left(n_+^s + n_-^s\right)d\ln n, \tag{1}$$

where n_+^s and n_-^s are, respectively, the numbers of cations and anions adsorbed (negatively) at the interface per unit area between the electrolyte solution and air, k is the Boltzmann constant and T is the absolute temperature. Let the adsorption potential, i.e., the work required to bring an ion from the bulk solution phase to a distance z from the interface be $W(z)$, which takes the same form for cations and anions for the case of symmetrical electrolytes. We thus find that:

$$n_\pm^s = n\int_0^\infty\left[\exp\left(-\frac{W(z)}{kT}\right) - 1\right]dz. \tag{2}$$

By integrating Eq. 1 after substituting Eq. 2, we obtain:

$$\gamma = \gamma_o - 2kT\int_0^n\int_0^\infty\left[\exp\left(-\frac{W(z)}{kT}\right) - 1\right]dzdn, \tag{3}$$

where γ_o is the surface tension of pure water in the absence of electrolyte ions. Following the theory of Levin and Flores-Mena [3], we assume that there formed an ion-free layer of thickness δ, which is the radius of hydrated electrolyte ions, just below the air–solution interface as shown in Fig. 1. This implies that we have assumed the same hydrated radius for cations and anions. Since the center of electrolyte ions cannot enter the ion-free layer region of pure water ($0 < z < \delta$), we have:

$$W(z) = \infty \text{ for } 0<z<\delta, \tag{4}$$

so that

$$\gamma = \gamma_o + 2nkT\delta - 2kT\int_0^n\int_\delta^\infty\left[\exp\left(-\frac{W(z)}{kT}\right) - 1\right]dzdn. \tag{5}$$

The expression for $W(z)$ for the region outside the ion-free layer ($z > \delta$) can be obtained by the method of Levin and Flores-Mena [3]. We first derive the potential distribution φ around an ion placed at $z = z_c$ ($z_c > \delta$). Let the relative permittivity of water be ε_r and that of air be ε_r' (≈ 1). In air ($z < 0$) and the ion-free layer region ($0 < z < \delta$) φ is given by the Laplace equation, whereas in the solution phase ($z > \delta$) we assume that φ satisfies the linearized Debye–Hückel equation:

$$\Delta\varphi = 0,\ z<0 \text{ and } 0<z<\delta, \tag{6}$$

$$\Delta\varphi - \kappa^2\varphi = -\frac{ve}{\varepsilon_r\varepsilon_o}\delta(z - z_c)\ , \mathrm{z} >\delta, \tag{7}$$

with:

$$\kappa = \left(\frac{2nv^2e^2}{\varepsilon_r\varepsilon_o kT}\right)^{1/2}, \tag{8}$$

where κ is the Debye–Hückel parameter, ε_o is the permittivity of a vacuum, e is the elementary electric charge, $\delta(z)$ is Dirac's delta function, and we have neglected the dependence of κ upon position z(1–5). It follows from the solution to Eqs. 6 and 7, subject to appropriate boundary conditions, that the contribution $\psi(z_c)$ from the interface to the potential felt by an ion fixed at $z = z_c$ is given by:

$$\psi(z_c) = \frac{ve}{4\pi\varepsilon_r\varepsilon_o}\int_0^\infty e^{-2p(z_c-\delta)}\frac{q\left\{\left(\varepsilon_r + \varepsilon_r'\right)(p - q)\exp(q\delta) + \left(\varepsilon_r - \varepsilon_r'\right)(p + q)\exp(-q\delta)\right\}}{p\left\{\left(\varepsilon_r + \varepsilon_r'\right)(p + q)\exp(q\delta) + \left(\varepsilon_r - \varepsilon_r'\right)(p - q)\exp(-q\delta)\right\}}dq \tag{9}$$

with:

$$p = \sqrt{q^2 + \kappa^2}. \tag{10}$$

The adsorption potential $W(z)$ is thus given by:

$$W(z) = \frac{v^2 e^2}{8\pi \varepsilon_r \varepsilon_o} \int_0^\infty e^{-2p(z-\delta)} \frac{q\left\{\left(\varepsilon_r + \varepsilon_r'\right)(p-q)\exp(q\delta) + \left(\varepsilon_r - \varepsilon_r'\right)(p+q)\exp(-q\delta)\right\}}{p\left\{\left(\varepsilon_r + \varepsilon_r'\right)(p+q)\exp(q\delta) + \left(\varepsilon_r - \varepsilon_r'\right)(p-q)\exp(-q\delta)\right\}} dq,\ z \geqslant \delta. \tag{11}$$

By substituting Eq. 11 into Eq. 5, one can calculate the surface tension of electrolyte solutions. Equation 5 reduces back to the following original Onsager–Samaras equation by setting δ to zero:

$$\gamma = \gamma_o - 2kT \int_0^n \int_0^\infty \left[\exp\left(-\frac{W(z)}{kT}\right) - 1\right] dz dn. \tag{12}$$

Let us call Eq. 5, as combined with Eq. 11, the modified Onsager–Samaras equation, since we have modified the original Onsager–Samaras Eq. 12 by taking into account the effect of the ion-free layer following Levin and Flores-Mena [3]. Equation 5, for low n, further gives the well-known Onsager–Samaras limiting law:

$$\gamma = \gamma_o + \frac{1}{2} v^2 \lambda_B nkT \left[\ln\left(\frac{2}{\kappa \lambda_B}\right) - 2\gamma_E + \frac{3}{2}\right] \tag{13}$$

with:

$$\lambda_B = \frac{e^2}{4\pi \varepsilon_r \varepsilon_o kT}, \tag{14}$$

where λ_B is the Bjerrum length, i.e., the distance between two elementary charges when their Coulomb interaction energy equals the thermal energy kT ($\lambda_B \approx 0.7$ nm for water at 25 °C) and γ_E is Euler's constant ($\gamma_E = 0.5772...$).

We next consider the theory of Levin and Flores-Mena [3], who were able to derive the following expression for the surface tension of an electrolyte solution without recourse to the Gibbs adsorption isotherm:

$$\gamma = \gamma_o + 2nkT\delta + 4n \int_0^1 \frac{d\lambda}{\lambda} \int_\delta^\infty \exp\left(-\frac{W(z)}{kT}\right) W(z) dz. \tag{15}$$

Here λ stands for a parameter expressing a stage of the Debye charging process, in which charge e in Eq. 11 is replaced by λe, λ being increased from 0 to 1.

Equations 5 and 15 are different from each other because of different approximations involved in the respective theories, despite the fact that in the thermodynamic limit they should be identical. Only in the limit of very small electrolyte concentrations, Eq. 15 tends to the Onsager–Samaras law (Eq. 13) [3].

Now we derive a simple expression for the surface tension that is consistent with both the theories of Onsager–Samaras [2] and Levin and Flores-Mena [3] for practically all electrolyte concentrations. We approximate:

$$\exp\left(-\frac{W(z)}{kT}\right) - 1 \approx -\frac{W(z)}{kT},\ z \geqslant \delta, \tag{16}$$

which is valid if:

$$\frac{W(z)}{kT} \ll 1,\ z \geqslant \delta. \tag{17}$$

This linearization approximation with respect to $W(z)$ is consistent with the usage of the linearized Debye-Hückel Eq. 7. Then Eq. 5 reduces to:

$$\gamma = \gamma_o + 2nkT\delta + 2\int_0^n \int_\delta^\infty W(z) dz dn \tag{18}$$

and Eq. 15 to:

$$\gamma = \gamma_o + 2nkT\delta + 4n \int_0^1 \frac{d\lambda}{\lambda} \int_\delta^\infty W(z) dz. \tag{19}$$

It can easily be shown that Eqs. 18 and 19 are identical with each other. The apparent difference between Eqs. 5 and 15 can thus be eliminated by linearizing exp ($-W(z)/kT$) with respect to $W(z)$.

Equation 18 (or Eq. 19) as combined with Eq. 11 can further be simplified into:

$$\gamma = \gamma_o + 2nkT\left[\delta + v^2 \lambda_B \left\{\frac{2\ln 2 - 1}{8} + f\left(\kappa\delta, \frac{\varepsilon_r'}{\varepsilon_r}\right)\right\}\right] \tag{20}$$

with:

$$f\left(\kappa\delta, \frac{\varepsilon_r'}{\varepsilon_r}\right) = \int_0^\infty \ln\left[1 + \left(\frac{1 - \varepsilon_r'/\varepsilon_r}{1 + \varepsilon_r'/\varepsilon_r}\right)\left(\sqrt{1+t^2} - t\right)^2 \exp(-2\kappa\delta t)\right] t dt. \tag{21}$$

On the right-hand side of Eq. 20, the term $2nkT\delta$ arises from the contribution from the ion-free layer, the second term $2nkTv^2\lambda_B(2\ln 2 - 1)/8$ from the image interaction between the electrolyte ions and the ion-free layer (as if the thickness of the latter were infinitely thick), and the last term $2nkT f(\kappa\delta, \varepsilon_r'/\varepsilon_r)$ from the image interaction between the electrolyte ions and air. Figure 2 shows $f(\kappa\delta, \varepsilon_r'/\varepsilon_r)$ as a function of $\kappa\delta$. Since the relative

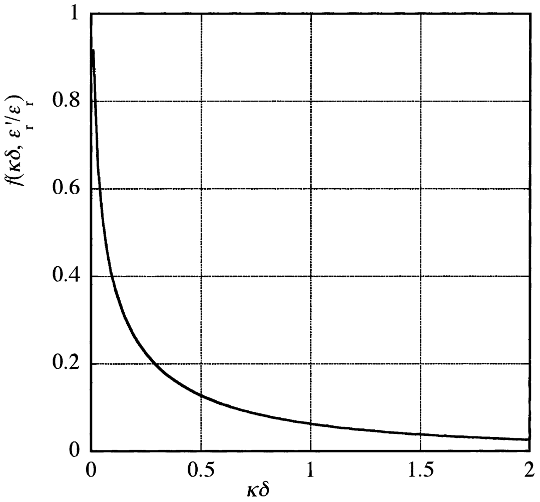

Fig. 2 $f(\kappa\delta, \varepsilon_r'/\varepsilon_r)$ plotted as a function of $\kappa\delta$, where κ is the Debye–Hückel parameter and δ is the thickness of an ion-free layer. $\varepsilon_r'/\varepsilon_r$ is set equal to 0

permittivity of water ($\varepsilon_r = 78.54$ at 25 °C) is much greater than that of air ($\varepsilon_r' \approx 1$), $\varepsilon_r'/\varepsilon_r$ is set equal to 0. It can be shown that $f(\kappa\delta, \varepsilon_r'/\varepsilon_r)$ tends to zero as $\kappa\delta$ increases, whereas $f(\kappa\delta, \varepsilon_r'/\varepsilon_r)$ tends to infinity as $\kappa\delta$ decreases. Although as $\kappa\delta$ decreases $f(\kappa\delta, \varepsilon_r'/\varepsilon_r)$ tends to infinity, its contribution to the excess surface tension ($2nkTf(\kappa\delta, \varepsilon_r'/\varepsilon_r)$) becomes zero as $\kappa\delta \to 0$. Also we find that:

$$\gamma = \gamma_o + 2nkT\left[\delta + v^2\lambda_B\left(\frac{2\ln 2 - 1}{8}\right)\right] \text{ for } \kappa\delta \to \infty. \tag{22}$$

In this limit, the excess surface tension, $\gamma - \gamma_o$, becomes exactly proportional to the electrolyte concentration n.

Comparison of various theories and experimental data for NaCl solution

The principal result of this paper is Eq. 20 for the surface tension of electrolyte solutions. In Fig. 3 we compare the present approximate result, Eq. 20 (curve 1) with the Levin and Flores-Mena theory, Eq. 15 (curve 2), the modified Onsager–Samaras theory, Eq. 5 (curve 3) as well as the experimental data for an aqueous NaCl solution ($v = 1$) at 25 °C [6]. We chose $\delta = 0.2125$ nm for NaCl, following Levin and Flores-Mena [3] and again set $\varepsilon_r'/\varepsilon_r$ to zero. These three results, all of which are essentially proportional to the electrolyte concentration, are all in good agreement with the experimental data in the concentration range up to as high as 1 M. In Fig. 3 we give also the original Onsagar–Samaras result, Eq. 12 (curve 4), which is seen to be much less than the experimental data and is applicable only for low electrolyte concentrations below 0.05 M. This is because the contribution of the ion-free layer dominates the excess surface tension, $2nkT\delta$, (curve 5, which is actually a straight line). We also see that the Levin and Flores-Mena theory and the modified Onsager–Samaras theory do not completely agree with each other but the numerical difference between them is seen to be negligibly small. This is again because of the dominant contribution of the ion-free layer.

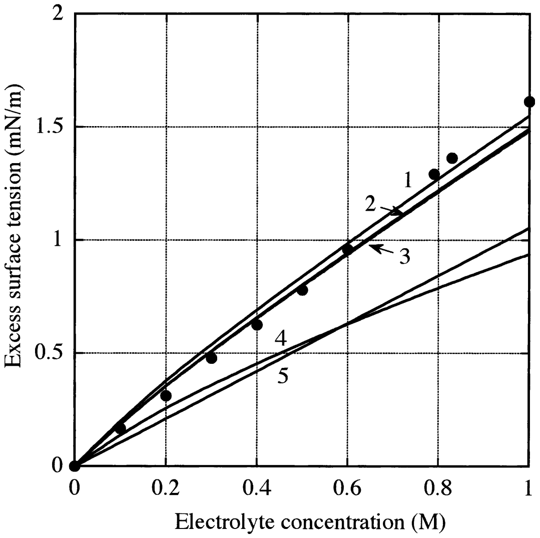

Fig. 3 Comparison of various theoretical results for the excess surface tension of NaCl solution at 25 °C ($\epsilon_r = 78.54$), $\gamma - \gamma_o$. The value of the thickness of the ion-free layer δ is chosen as 0.2125 nm following Levin and Flores-Mena [3]. *Curve 1*, the present result (Eq. 20); *curve 2*, Levin and Flores-Mena Eq. 20; *curve 3*, the modified Onsager–Samaras Eq. 5; *curve 4*, the original Onsager–Samaras Eq. 12; *curve 5*, the contribution of the ion-free layer ($2nkT\delta$). *Filled circles* are the experimental data for NaCl from [6]. ϵ_r'/ϵ_r is set equal to 0

Our result, Eq. 20, which is based on linearization approximation with respect to $W(z)$ (see also [7]), is consistent with both of the canonical and grand canonical approaches. This linearization, which is consistent with the linearized Debye–Hückel Eq. 7, is allowed only if condition 17 holds. Note that for finite δ, condition 17 holds for practically all z ($\geq\delta$) and all electrolyte concentrations for the present case.

The observed nearly linear dependence of the excess surface tension upon the electrolyte concentration, as is seen in Fig. 3, suggests introduction of the concept of the effective thickness of the ion-free layer formed at the water–electrolyte solution interface, which becomes larger than the radius of actual hydrated ion itself due to the effects of the image interactions between electrolyte ions and the ion-free layer and those between electrolyte ions and air. If one rewrites Eq. 20 as:

$$\gamma = \gamma_o + 2nkT\delta_{\text{eff}}, \tag{23}$$

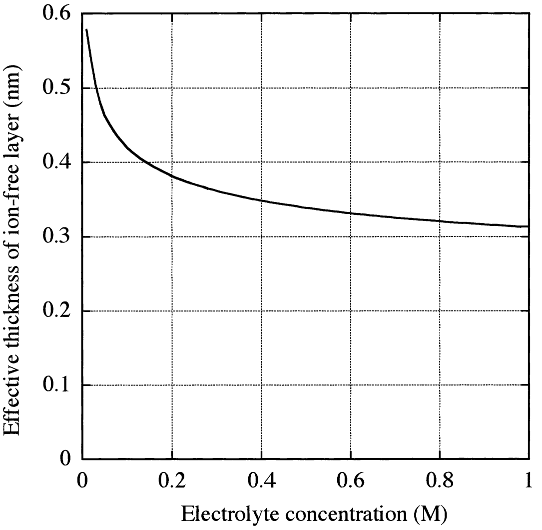

Fig. 4 Effective thickness δ_{eff} of an ion-free layer of thickness δ calculated with Eq. 24 for an aqueous NaCl solution at 25 °C ($\delta = 0.2125$ nm). $\varepsilon_r'/\varepsilon_r$ is set equal to 0

then we can see that the effective thickness δ_{eff} of the ion-free layer is given by:

$$\delta_{\mathrm{eff}} = \delta + v^2\lambda_{\mathrm{B}}\left\{\frac{2\ln 2 - 1}{8} + f\left(\kappa\delta, \frac{\varepsilon_r'}{\varepsilon_r}\right)\right\}. \tag{24}$$

Figure 4 shows the effective thickness δ_{eff} calculated via Eq. 24 as a function of the electrolyte concentration n for an aqueous NaCl solution at 25 °C ($\delta = 0.2125$ nm and $v = 1$), $\varepsilon_r'/\varepsilon_r$ being set to zero. We see that δ_{eff} deceases as the electrolyte concentration increase, tending to $\delta + v^2\lambda_{\mathrm{B}}(2\ln 2 - 1)/8$ (which is electrolyte-concentration-independent and amounts to 0.247 for $v = 1$) in the very high concentration. In this limit, the excess surface tension arises only from the image interaction between the electrolyte ions and the ion-free layer (as if the thickness of the latter were infinitely thick).

Conclusion

We have derived a simple analytic equation (Eq. 20) for the surface tension of electrolyte solutions, which is in good agreement with the experimental data on NaCl in the concentration range up to as high as 1 M. This expression is consistent with the recent theory of Levin and Flores-Mena (canonical approach) [3] and the Onsager–Samaras theory (grand canonical approach) [2] modified by taking into account the ion-free layer effect. It is shown that the excess surface tension consists of contributions of the ion-free layer, the image interaction between the electrolyte ions and the ion-free layer, and the image interaction between the electrolyte ions and air.

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