Colloid Polym Sci (2004) 283: 119–124
DOI 10.1007/s00396-004-1114-3

ORIGINAL CONTRIBUTION

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Surface tension of general electrolyte solutions

Received: 23 February 2004
Accepted: 16 March 2004

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Abstract A simple analytic expression is derived for the surface tension of a solution of general electrolytes including symmetrical and unsymmetrical electrolytes. Following the theory of Levin and Flores-Mena (Europhys Lett (2001) 56:187), we have introduced an ion-free layer of thickness δ just below the Gibbs dividing surface at the air/electrolyte solution interface. We use the linearized Poisson-Boltzmann equations for the mean potential and for the local fluctuation potential around an ion in the electrolyte solution, together with the Laplace equation for these potentials in the ion-free layer. It is found that the contribution of the mean potential as well as the tangential Maxwell stress along the interface vanishes for low potentials. Experimental data by Matubayasi et al (J Colloid Interf Sci (1999) 209:398, ibid (1999) 209:403, ibid (2001) 243:444) are analyzed with the present theory in order to estimate the values of δ for several electrolytes.

Keywords Surface tension · General electrolyte · Ion-free layer

Introduction

The surface tension of water in contact with air is increased when an electrolyte is added to the water phase. Wagner [1] and Onsager and Samaras [2] showed that this surface tension increase is caused by negative adsorption (depletion) of electrolyte ions at the air/water interface due to the electrostatic repulsive interaction between ions and their images with respect to the air/water interface. Agreement with experiment, however, is good only at very low electrolyte concentrations. Various improvements on the theory of Onsager and Samaras have been attempted [3, 4, 5, 6, 7, 8, 9] (see also a review by Randles [10]). In particular, Schmutzer [3] introduced an ion-free layer of thickness δ at the air/water interface, represented by an infinite potential barrier at a distance δ from the air/water interface.Böstrom et al considered dispersion forces between ions and the air/water interface [6]. Levin and Flores-Mena [7, 8] employed the concept of the ion-free layer by regarding δ as the radius of the hydrated electrolyte ions, and obtained the change in the local fluctuation potential due to the presence of the air/water interface by solving the Laplace equation in the region inside the ion-free layer and the Poisson-Boltzmann equation in the region below the ion-free layer. They showed [7] that the presence of the ion-free layer causes a large increase in surface tension, resulting in excellent agreement with experimental data for NaCl solutions from Matubayasi et al [11]. On the basis of the theory of Levin and Flores-Mena [7], Ohshima and Matsubara [9] have recently derived a simple analytic expression for the surface tension increase, which is applicable not only to the air/water interface but also to the interface between two arbitrary media.

The purpose of the present paper is to extend the theory of Levin and Flores-Mena [7], who treated symmetrical electrolytes, to cover general electrolytes including unsymmetrical electrolytes. For symmetrical electrolytes, the potential energy of the image interaction is equal for cations and anions. As was demonstrated by Bell and Rangecroft [5], however, for unsymmetrical electrolytes, the image interaction energy is no longer equal for cations and anions, which gives rise to a non-zero volume charge density in the electrolyte solution near the air/water interface, producing a mean potential (which vanishes for symmetrical electrolytes). The depletion of ions near the interface, which results in the surface tension increase, is therefore influenced by this mean potential. The mean potential also produces the tangential Maxwell stress along the interface, affecting the surface tension. In the present paper, however, we show that the contribution of the mean potential to the surface tension vanishes for low potentials. We analyze experimental data by Matubayasi et al [11, 12, 13, 14] in order to estimate the values of the thickness δ of the ion-free layer for various electrolytes.

Surface tension of an electrolyte solution

Consider the surface tension γ of an electrolyte solution. Let the electrolyte be composed of N ionic species of valence v_i and bulk concentration (number density) n_i ($i=1,2,...,N$). 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. We start with the Gibbs adsorption isotherm,

$$d\gamma = -kT\sum_{i=1}^{N} n_i^{s} d\ln n_i \tag{1}$$

with

$$n_i^{s} = n_i\int_0^{\infty}\left[\exp\left(-\frac{v_i e\phi(z)+W_i(z)}{kT}\right)-1\right]dz \tag{2}$$

where $n^{s}{}_i$ is the number of ions of species i adsorbed (negatively) at the interface per unit area between the electrolyte solution and air, e is the elementary electric charge, k is the Boltzmann constant, T is the absolute temperature, $\phi(z)$ is the mean potential, and $W_i(z)$ is the additional potential energy of an ion of the species i at position z resulting from the change in the local fluctuation potential ψ_i due to the presence of the air/water interface, which is given by

$$W_i(z) = \frac{1}{2}v_i e\psi_i(z) \tag{3}$$

with

$$\psi_i = \lim_{r\to 0}\left[\varphi_i - \frac{v_i e}{4\pi\varepsilon_r\varepsilon_0 r}\right] \tag{4}$$

where r is the distance measured from the center of the ion. Here, the potential ψ_i, which eliminates the Coulomb potential produced by the ion itself, is the potential of the field acting on the ion due to the other ions. By integrating Eq. 1 after substituting Eq. 2, we obtain

$$\gamma = \gamma_0 - kT\sum_{i=1}^{N}\int_0^{n_i}\int_0^{\infty}\left[\exp\left(-\frac{v_i e\phi(z)+W_i bigg(z)}{kT}\right)-1\right]dzdn_i \tag{5}$$

where γ_0 is the surface tension of pure water in the absence of electrolyte ions. Following the theory of Levin and Flores-Mena [7], we assume that an ion-free layer formed just below the Gibbs dividing surface at the air/solution interface, as shown in Fig. 1. We denote the thickness of the ion-free layer by δ, which corresponds to the average radius of hydrated electrolyte ions. Since the center of the electrolyte ions cannot enter the ion-free layer region of pure water ($0<z<\delta$), we have

$$W_i(z) = \infty \text{ for } 0<z<\delta, \tag{6}$$

so that

$$\gamma = \gamma_0 + kT\delta\sum_{i=1}^{N} n_i - kT\sum_{i=1}^{N}\int_0^{n_i}\int_\delta^{\infty}\left[\exp\left(-\frac{v_i e\phi(z)+W_i(z)}{kT}\right)-1\right]dzdn_i. \tag{7}$$

Further, we linearize the integrand in the last term on the right hand side of Eq. 7 with respect to $\phi(z)$ and $W_i(z)$ [15], viz,

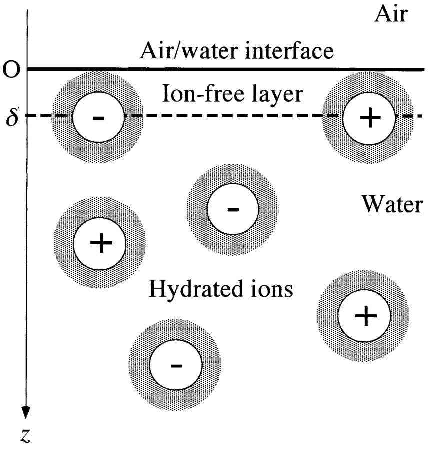

Fig. 1 The model of Levin and Flores-Mena [7] for the interface between an electrolyte solution and air at $z=0$. An ion-free layer of thickness δ, corresponding to the average radius of hydrated ions, is formed just below the Gibbs dividing surface at the air/solution interface. Hydration of ions prevents their centers from coming closer than δ to the air/solution interface

$$\exp\left(-\frac{v_i e\phi(z) + W_i(z)}{kT}\right) - 1 = -\frac{v_i e\phi(z) + W_i(z)}{kT} \tag{8}$$

which is valid if

$$\frac{|v_i e\phi(z) + W_i(z)|}{kT} \ll 1. \tag{9}$$

Then, Eq. 7 becomes

$$\begin{aligned}\gamma &= \gamma_0 + kT\delta\sum_{i=1}^{N} n_i + \sum_{i=1}^{N}\int_0^{n_i}\int_\delta^\infty [v_i e\phi(z) + W_i(z)]dzdn_i \\ &= \gamma_0 + kT\delta\sum_{i=1}^{N} n_i + \sum_{i=1}^{N}\int_0^{n_i}\int_\delta^\infty W_i(z)dzdn_i,\end{aligned} \tag{10}$$

where we have utilized the electroneutrality condition $\Sigma v_i n_i = 0$. We therefore see that the contribution from the mean potential $\phi(z)$ can be neglected as long as linearization of Eq. 8 is allowed. Also, the contribution of the tangential Maxwell stress $\frac{1}{2}\varepsilon_r\varepsilon_0\left(\frac{d\phi}{dz}\right)^2$ can be neglected in this linearization approximation.

The expression for $W_i(z)$ for the region outside the ion-free layer ($z > \delta$) was obtained in a previous paper [9] by the method of Levin and Flores-Mena [7]. We first derive the local fluctuation potential ϕ_i around an ion of species i placed at $z = z_c (z_c > \delta)$. Let the relative permittivity of water be ϵ_r and that of air be $\epsilon_r'(\approx 1)$. In air ($z < 0$) and the ion-free layer region ($0 < z < \delta$), ϕ_i obeys the Laplace equation, whereas in the solution phase ($z > \delta$) we assume that ϕ_i satisfies the linearized Poisson-Boltzmann equation, viz,

$$\Delta\varphi_i = 0,\ z<0 \text{ and } 0<z<\delta, \tag{11}$$

$$\Delta\varphi_i - \kappa^2\varphi_i = -\frac{v_i e}{\varepsilon_r\varepsilon_0}\delta(z - z_c),\ z > \delta, \tag{12}$$

with

$$\kappa = \left(\frac{\sum_{i=1}^{N} n_i v_i^2 e^2}{\varepsilon_r\varepsilon_0 kT}\right)^{1/2}, \tag{13}$$

where κ is the local Debye-Hückel parameter, ϵ_0 is the permittivity of a vacuum, and $\delta(z)$ is Dirac's delta function. Here we neglect the dependence of κ upon position z [1, 2, 3, 4, 5, 6, 7, 8, 9]. It follows from the solution ϕ_i to Eqs. 11 and 12, subject to appropriate boundary conditions, that the contribution $\psi_i(z_c)$ (Eq. 4) from the interface to the potential felt by an ion of species i fixed at $z = z_c$ is obtained with the help of Eq. 4 as [9],

$$\psi_i(z_c) = \frac{v_i e}{4\pi\varepsilon_r}\varepsilon_0\int_0^\infty e^{-2p(z_c-\delta)} \frac{q\{(\varepsilon_r + \varepsilon_r')(p-q)\exp(q\delta) + (\varepsilon_r - \varepsilon_r')(p+q)\exp(-q\delta)\}}{p\{(\varepsilon_r + \varepsilon_r')(p+q)\exp(q\delta) + (\varepsilon_r - \varepsilon_r')(p-q)\exp(-q\delta)\}} \times dq \tag{14}$$

with

$$p = \sqrt{q^2 + \kappa^2} \tag{15}$$

The potential energy $W_i(z)$ is therefore given by (using Eq. 3):

$$W_i(z) = \frac{v_i^2 e^2}{8\pi\varepsilon_r}\varepsilon_0\int_0^\infty e^{-2p(z-\delta)} \frac{q\{(\varepsilon_r + \varepsilon_r')(p-q)\exp(q\delta) + (\varepsilon_r - \varepsilon_r')(p+q)\exp(-q\delta)\}}{p\{(\varepsilon_r + \varepsilon_r')(p+q)\exp(q\delta) + (\varepsilon_r - \varepsilon_r')(p-q)\exp(-q\delta)\}} \times dq,\ (z \geqslant \delta). \tag{16}$$

Equation 10, when combined with Eq. 16, can further be simplified into

$$\gamma = \gamma_0 + kT\left[\delta\sum_{i=1}^{N} n_i + \left(\sum_{i=1}^{N} v_i^2 n_i\right) \times \lambda_B\left\{\frac{2\ln 2 - 1}{8} + f(\kappa\delta, \varepsilon_r'/\varepsilon_r)\right\}\right] \tag{17}$$

with

$$f(\kappa\delta, \varepsilon_r'/\varepsilon_r) = \int_0^\infty \ln\left[1 + \left(\frac{1 - \varepsilon_r'/\varepsilon_r}{1 + \varepsilon_r'/\varepsilon_r}\right) \left(\sqrt{1+t^2} - t\right)^2 \exp(-2\kappa\delta t)\right] tdt, \tag{18}$$

$$\lambda_B = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 kT} \tag{19}$$

where λ_B is the Bjerrum length. Equation 17 is the required expression for the surface tension of general electrolyte solutions.

Expressions for γ for several electrolytes are explicitly given below.

a. 1–1 electrolyte of concentration n:

$$\gamma = \gamma_0 + nkT\left[2\delta + 2\lambda_B\left\{\frac{2\ln 2 - 1}{8} + f(\kappa\delta, \varepsilon_r'/\varepsilon_r)\right\}\right] \tag{20}$$

with $\kappa = (2ne^2/\varepsilon_r\varepsilon_0 kT)^{1/2}$.

b. 2–1 (or 1–2) electrolyte of concentration n:

$$\gamma = \gamma_0 + nkT\left[3\delta + 6\lambda_B\left\{\frac{2\ln 2 - 1}{8} + f\left(\kappa\delta, \varepsilon_r'/\varepsilon_r\right)\right\}\right] \tag{21}$$

with $\kappa = \left(6ne^2/\varepsilon_r\varepsilon_0 kT\right)^{1/2}$.

c. 2–2 electrolyte of concentration n:

$$\gamma = \gamma_0 + nkT\left[2\delta + 8\lambda_B\left\{\frac{2\ln 2 - 1}{8} + f\left(\kappa\delta, \varepsilon_r'/\varepsilon_r\right)\right\}\right] \tag{22}$$

with $\kappa = \left(8ne^2/\varepsilon_r\varepsilon_0 kT\right)^{1/2}$.

d. 3–1 (or 1–3) electrolyte of concentration n:

$$\gamma = \gamma_0 + nkT\left[4\delta + 12\lambda_B\left\{\frac{2\ln 2 - 1}{8} + f\left(\kappa\delta, \varepsilon_r'/\varepsilon_r\right)\right\}\right] \tag{23}$$

with $\kappa = \left(12ne^2/\varepsilon_r\varepsilon_0 kT\right)^{1/2}$.

e. Mixed solution of 1–1 electrolyte of concentration n_1 and 2–1 electrolyte of concentration n_2:

$$\gamma = \gamma_0 + kT\Bigg[(2n_1 + 3n_2)\delta + \left(2n_1 + 6n_2\right) \lambda_B\left\{\frac{2\ln 2 - 1}{8} + f\left(\kappa\delta, \varepsilon_r'/.\varepsilon_r\right)\right\}\Bigg] \tag{24}$$

with $\kappa = \left[(2n_1 + 6n_2)e^2/\varepsilon_r\varepsilon_0 kT\right]^{1/2}$.

In Eqs. 20–24, the concentration n is given in units of m^{-3}. The electrolyte concentration c (M), which is expressed in units of M, is related to $n\,(\mathrm{m}^{-3})$ by $n = 1000N_A c$, N_A being Avogadro's number.

Finally we give the following simple interpolation formula for $f(\kappa\delta,\ \epsilon_r'/\epsilon_r)$ (see Eq. 18) for the case of an air/water interface at 25 °C ($\epsilon_r' = 1$ and $\epsilon_r = 78.54$):

$$f\left(\kappa\delta, \frac{1}{78.54}\right) = 0.0996 \times \ln\left[0.9288 + \frac{0.5365}{\kappa\delta} + \frac{0.3741}{(\kappa\delta)^2}\right] \tag{25}$$

with relative errors less than 1% for 0.15 nm ≤ δ ≤ 1 nm. For very small δ, Eq. 9 does not hold, so that Eqs. 18 and 25 become invalid.

Estimation of the thickness of the ion-free layer

One can calculate the increase in surface tension at an air/water interface when electrolytes are added to the water phase for a given value of the thickness of the ion-free layer δ using Eq. 17. It is therefore possible to estimate the value of δ for an electrolyte solution by comparing theoretical results calculated via Eq. 17 and experimental data for the surface tension increase. We have analyzed experimental data for $MgCl_2$ at 25 °C from Matubayasi et al [11] and found that the experimental data for $MgCl_2$ are described well by a theoretical curve with $\delta = 0.29$ nm using a curve-fitting procedure. Figure 2 shows the experimental data from Matubayasi et al [11], together with the best-fit curve for $\delta = 0.29$ nm.

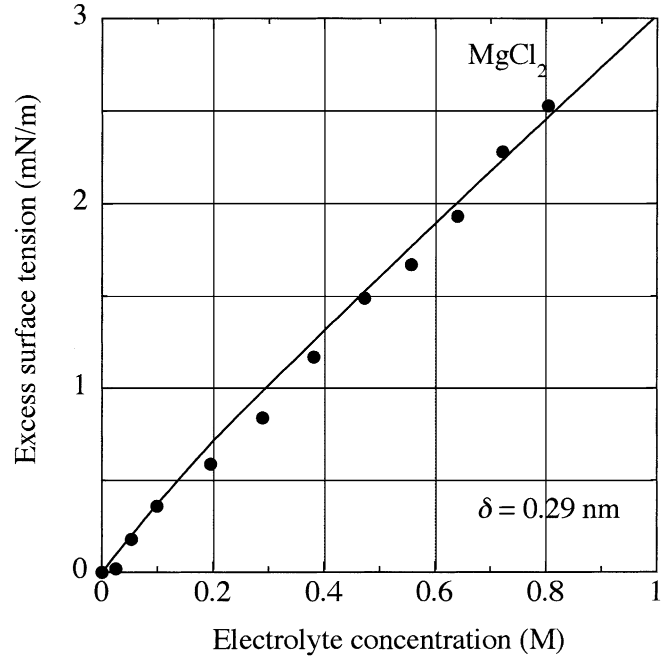

Fig. 2 Comparison between theoretical results for the excess surface tension of $MgCl_2$ solution at 25 °C ($\epsilon_r = 78.54$ and $\epsilon_r' = 1$); $\Delta\gamma = \gamma - \gamma_o$, calculated via Eq. 17, and the experimental results from Matubayasi et al [11] given by circles. The best-fit value of the thickness of the ion-free layer δ is found to be $\delta = 0.29$ nm, which is shown by a solid curve

As is seen in Fig. 2, the surface tension increase $\Delta\gamma = \gamma - \gamma_0$ as a function of electrolyte concentration c may be expressed by a straight line with constant slope $d\Delta\gamma/dc$. This suggests a simple approximate estimation for δ without a curve-fitting procedure. That is, theoretical and experimental values of $d\Delta\gamma/dc$ are compared after approximating both theoretical and experimental values of $\Delta\gamma$ as linear functions of c. We found that theoretical values of $d\Delta\gamma/dc$ are approximated quite well by the values of $d\Delta\gamma/dc$ for $c = 0.8$ M. That is, at 25 °C ($\epsilon_r' = 1$ and $\epsilon_r = 78.54$), we have found that for 1–1 electrolytes at 0.15 nm ≤ δ ≤ 1 nm

$$\frac{d\Delta\gamma}{dc} = 0.1708 + 4.9579 \times \delta + 0.3524 \times \ln\left(0.9288 + \frac{0.1825}{\delta} + \frac{0.0433}{\delta^2}\right), \mathrm{(mN/m/M)} \tag{26}$$

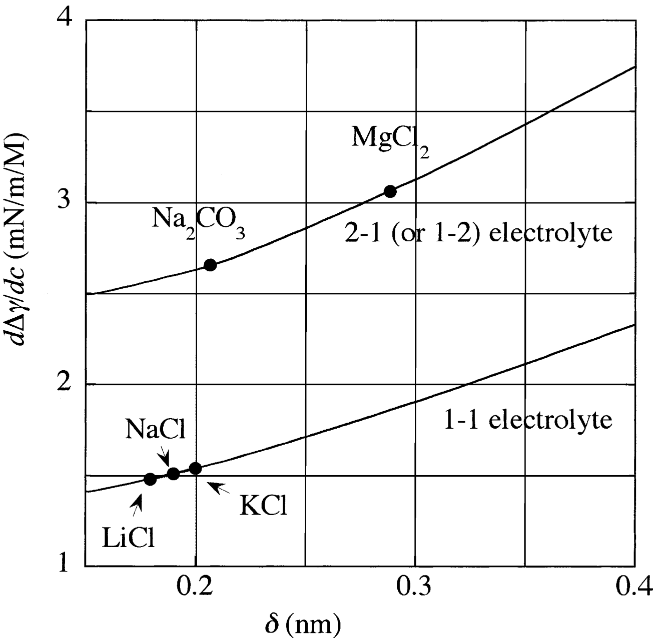

Fig. 3 Theoretical results for five kinds of electrolytes (LiCl, NaCl, KCl, Na_2CO_3, and $MgCl_2$) at 25 °C ($\epsilon_r = 78.54$ and $\epsilon_r' = 1$). Solid lines are theoretical curves for $d\Delta\gamma/dc$, where the lower curve corresponds to 1–1 electrolytes (Eq. 26) and the upper curve to 2–1 (or 1–2) electrolytes (Eq. 27). Experimental values for $d\Delta\gamma/dc$ from Matubayasi et al [11, 12, 13, 14] are plotted using circles on the lower or upper curve, depending on whether the electrolyte type is 1–1 or 2–1 (or 1–2). The value for the abscissa of each circle gives the value of δ for the corresponding electrolyte; these values are found to be 0.18 nm for LiCl, 0.19 nm for NaCl, 0.20 nm for KCl, 0.21 nm for Na_2CO_3, and 0.29 nm for $MgCl_2$

and for 2–1 (or 1–2) electrolytes at 0.15 nm ≤ δ ≤ 1 nm

$$\frac{d\Delta\gamma}{dc} = 0.5125 + 7.4369 \times \delta + 1.0571 \times \ln\left(0.9288 + \frac{0.1054}{\delta} + \frac{0.0144}{\delta^2}\right), (\mathrm{mN/m/M}). \tag{27}$$

In Eqs. 26 and 27, $\Delta\gamma$ is given in units of mN/m, c in units of M, and δ in units of nm.

We have analyzed experimental data from Matubayasi et al [11, 12, 13, 14] in order to estimate the thickness of the ion-free layer δ for several electrolytes. Figure 3 shows results for five kinds of electrolytes (NaCl, LiCl, KCl, Na_2CO_3 and $MgCl_2$), in which the solid lines are theoretical curves for $d\Delta\gamma/dc$, and the lower curve corresponds to 1–1 electrolytes (Eq. 26) and the upper curve to 2–1 (or 1–2) electrolytes (Eq. 27). Experimental values of $d\Delta\gamma/dc$ for five kinds of electrolytes are plotted using circles on the lower or upper curve, depending on whether the electrolyte type is 1–1 or 2–1 (or 1–2). The value of the abscissa for each circle gives the value of δ for the corresponding electrolyte. The values of δ estimated in this way are 0.18 nm for LiCl, 0.19 nm for NaCl (which is 10% smaller than the value of $\delta = 0.2125$ nm employed by Levin and Flores-Mena [7]), 0.20 nm for KCl, 0.21 nm for Na_2CO_3, and 0.29 nm for $MgCl_2$. These values of δ are similar to the values for the hydration radii of electrolyte ions [16].

Conclusions

We have derived a simple analytic formula (Eq. 17) for the surface tension of general electrolyte solutions, which accounts for the contribution of the ion-free layer formed just below the Gibbs dividing surface at the air/electrolyte solution interface, and that of the image interaction of electrolyte ions. A simple interpolation formula for the latter is given (Eq. 25). The surface tension formula obtained (Eq. 17) is also applicable to the interfacial tension between two arbitrary media. It is found that the contribution of the mean potential as well as the tangential Maxwell stress along the interface vanishes for low potentials. It is possible to estimate the values of δ by analyzing experimental data. Simple interpolation formula (Eqs. 26 and 27) are derived for $d\Delta\gamma/dc$, which is nearly constant both experimentally and theoretically.

Acknowledgements We thank Prof. N. Matubayasi of Nagasaki University for kindly providing us with the original data for the surface tension of $MgCl_2$ (the data given in [11] are based on these data).

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