

Surface tension for aqueous electrolyte solutions by the modified mean spherical approximation

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Received 25 January 2000; accepted 1 June 2000

Abstract

The concentration dependence of the surface tension of single and mixed electrolyte aqueous solutions is studied, based on the assumption that the surface layer can be treated as a separate phase located between vapor and bulk liquid phases. The mean spherical approximation modified by Lu et al. [J.-F. Lu, Y.-X. Yu, Y.-G. Li, *Fluid Phase Equilibria* 85 (1993) 81–100] is used to calculate the activity coefficients of water in the surface and bulk liquid phases. The relation between the electrolyte concentration in the surface and bulk liquid phases is established and only one parameter needs to be determined. The surface tensions for 31 single electrolyte aqueous solutions are correlated and the overall average absolute deviation is 0.70%. The surface tensions at different temperatures are predicted with the parameters obtained at one fixed temperature. By introducing the proper mixing rules, the surface tensions for 14 mixed electrolyte aqueous solutions are predicted without any mixing parameters, and the total average absolute deviation is 0.63%. All the calculated results are compared with that of the surface tension model for aqueous electrolyte solutions proposed by Li et al. [Z.-B. Li, Y.-G. Li, J.-F. Lu, *Ind. Eng. Chem. Res.* 38 (1999) 1133–1139]. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Model; Surface tension; Modified mean spherical approximation; Electrolyte solution; Activity coefficient; Osmotic coefficient

1. Introduction

The surface tension of aqueous electrolyte solutions has a great influence in the mass and heat transfers across interfaces. It is required in many fields including separation processes and environmental engineering [1]. To meet these engineering requirements, an accurate estimation method must be developed because surface tension data for electrolyte solutions over a wide range concentration and temperature are scarce.

The surface tension of non-electrolyte solutions have been investigated by several workers [1–4], whereas for electrolyte solutions, many investigations were limited to low concentration solutions. Oka

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[5] derived a quantitative limiting model of surface tension for strong electrolyte solutions. Considering the ions to be homogeneously distributed in the solutions, Ariyama [6,7] obtained a theory of surface tension for the dilute solutions. By solving the Debye–Hückel equation in the Wagner–Kirkwood–Buff (WKB) approximation [8], Nakamura et al. [9] obtained the ion distribution near the surface of electrolyte solutions and compared the calculated surface tension change with the experimental values. Stairs [10] modified the Onsager–Sarnaras expression to include ion-induced dipole term in the image potential, and effective solvated ionic polarizabilities were used. Bhuiyan et al. [11] studied the surface tension of aqueous electrolyte within the framework of the primitive model of the planar electric double layer, the surface being treated as a hard wall of relative permittivity unity. In their work, the structure of the model interface was described by the modified Poisson–Boltzmann (MPB) approximation [12], and only 1:1 and 2:2 valency systems with the molarity lower than 2 mol/l were investigated. Recently, Li et al. [13] proposed a surface tension model for concentrated electrolyte aqueous solutions, and the relation between the surface tensions and the osmotic coefficients of electrolyte solutions, which were calculated by the Pitzer equation [14], was established. The surface tensions of 46 single electrolyte solutions were correlated with acceptable deviations. But in the high concentration region, the correlation of Li et al. [13] overestimates the surface tensions when compared with the experimental values. Therefore, the estimations of the surface tension for concentrated electrolyte solutions require to be studied further.

In this work, we present the concentration dependence of the surface tension of single and mixed electrolyte aqueous solutions at different temperatures. The modified mean spherical approximation (MSA) [15] has been used to calculate osmotic coefficients of surface and bulk liquid phases. A relation of molality between surface and bulk liquid phases is established. Comparisons of the present model with that of Li et al. [13] are carried out.

2. Theory

2.1. General equation for surface tension of single electrolyte solution

When the surface layer is assumed to be a phase separate from the bulk liquid phase, the chemical potentials of water in the bulk liquid and surface phases of an electrolyte solution are given by

$$\mu_w^B = \mu_w^{0B} + RT \ln a_w^B \quad (1)$$

$$\mu_w^S = \mu_w^{0S} + RT \ln a_w^S - \sigma \bar{A}_w \quad (2)$$

where a_w is the activity of water, σ the surface tension of the electrolyte solution, \bar{A}_w the partial molar surface area, the subscript w refers to water, and the superscripts B and S refer to the bulk liquid phase and surface phase, respectively. By using the condition of phase equilibrium, the following equation can be obtained [1,13]:

$$\sigma \bar{A}_w = \sigma_w A_w + RT \ln \left(\frac{a_w^S}{a_w^B} \right) \quad (3)$$

where A_w is the molar surface area of water.

It is assumed in previous works [2–4,13] that

$$\bar{A}_w = A_w \quad (4)$$

which reduces Eq. (3) to

$$\sigma = \sigma_w + \frac{RT}{A_w} \ln \frac{a_w^S}{a_w^B} \quad (5)$$

The activity of water in a single electrolyte solution can be calculated from the osmotic coefficient by

$$\ln a_w = -\frac{\nu m \phi}{55.51} \quad (6)$$

where $\nu = \nu_+ + \nu_-$. From Eqs. (5) and (6), the surface tension of a single electrolyte solution can be expressed as

$$\sigma = \sigma_w + \frac{\nu RT}{55.51 A_w} (m^B \phi^B - m^S \phi^S) \quad (7)$$

Application of Eq. (7) requires knowledge of: (i) the molar surface area and the surface tension of water; (ii) the molality of an electrolyte in the surface phase and (iii) a model for calculating the osmotic coefficients in the surface and bulk liquid phases.

2.2. Molar surface area and surface tension of water

The surface tensions of electrolyte solutions calculated from Eq. (7) are more sensitive to the values of the molar surface area of water than to the values of the osmotic coefficients. Li et al. [13] calculated the molar surface area of water from the molar volume of pure water, as a result the calculated surface tensions of 1:2 valency systems are always lower than the experimental values in the low concentration region. Nath [1] tested two techniques for calculation of molar surface areas, based on Paquette areas and Rasmussen areas [2]. It was found that use of Rasmussen areas resulted in a vastly improved fit to the experimental surface tensions for aqueous non-electrolyte solutions [1,2]. For aqueous electrolyte solutions, Rasmussen area [2] of water was adopted in our calculation, i.e.

$$A_w = 7.225 \times 10^7 \text{ cm}^2/\text{mol} \quad (8)$$

As for the surface tension of pure water at different temperatures, the data from a compilation by Vargaftik [16] were used in this work.

2.3. Molality of electrolyte in surface phase

The molality ratio between the surface and bulk liquid phases can be defined as

$$g = \frac{m^S}{m^B} \quad (9)$$

Li et al. [13] considered g as a proportional constant. This assumption is not proper at high concentration because when $x_w \rightarrow 0$, both the surface and bulk liquid phases become pure electrolyte, and g tends to unity. In this work, the surface phase is assumed to be neutral and the parameter g is treated as a function of the bulk liquid molality. The following expression can be used to represent g :

$$g = 1 - \beta x_w^2 \quad (10)$$

where β is a constant to be determined and the mole fraction of water in the bulk liquid phase can be expressed as

$$x_w = \frac{55.51}{55.51 + \nu m^B} = \frac{1}{1 + (\nu m^B/55.51)} \quad (11)$$

From Eqs. (10) and (11), the following expression can be obtained:

$$g = 1 - \frac{\beta}{[1 + (\nu m^B/55.51)]^2} = 1 - \frac{\beta}{1 + (2\nu m^B/55.51) + (\nu m^B/55.51)^2} \quad (12)$$

For aqueous electrolyte solutions, when the concentration is not very high, the term $(\nu m^B/55.51)^2$ is small and was neglected in this work. Then Eq. (12) reduces to

$$g = 1 - \frac{\beta}{[1 + (\nu m^B/55.51)]} \quad (13)$$

When the solution is infinite dilution, the concentration of electrolyte in both bulk liquid phase and surface phase will tend to zero, and the ratio g should be a constant. The parameter β can be determined by fitting the experimental surface tensions of the single electrolyte solution. Therefore, the molality of electrolyte in the surface phase can be calculated by

$$m^S = m^B \left[1 - \frac{\beta}{[1 + (\nu m^B/55.51)]} \right]$$

2.4. The osmotic coefficient from the modified mean spherical approximation

Several methods can be used to calculate the properties of electrolyte solutions. Perhaps the commonly used method is the Pitzer equation [14,17]. Recently, Taghikhani and Vera [18] used a Kelvin hard sphere-mean spherical approximation (K-MSA) model to correlate the activity coefficient in electrolyte solutions. Gao et al. [19] combined the non-primitive MSA with the perturbation theory to calculate the activity coefficient and solubility of gas in the electrolyte solutions. In their study [19], the maximum concentration of electrolyte in the solution is 6 mol/kg. Lu et al. [15] modified the primitive MSA and applied it to the calculation of the activity coefficients for electrolyte solutions up to high concentration. The modified MSA [15] proves to be very accurate for 85 single electrolyte solutions. In this work, the modified MSA [15] was adopted to calculate the activity coefficients and the osmotic coefficients were obtained by the integral of Gibbs–Duhem equation.

In the Modified MSA, the expression for the activity coefficients is a sum of an electrostatic and a hard-sphere term

$$\ln \gamma_i = \ln \gamma_i^{\text{elec}} + \ln \gamma_i^{\text{hs}} \quad (15)$$

The first term in Eq. (15) can be expressed as [20]

$$\ln \gamma_i^{\text{elec}} = \frac{z_i e^2 M_i}{DkT} - \frac{P_n d_i}{4\Delta} \left(\Gamma a_i + \frac{\pi}{12\Delta} \alpha^2 P_n d_i^2 \right) \quad (16)$$

where

$$\alpha^2 = \frac{4\pi e^2}{DkT}$$

$$\xi_n = \frac{\pi}{6} \sum_{k=1}^N \rho_k d_k^n \quad (n = 0, 1, 2, 3)$$

$$\Delta = 1 - \xi_3$$

$$P_n = \frac{1}{\Omega} \sum_{k=1}^N \frac{\rho_k d_k z_k}{1 + \Gamma d_k}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_{k=1}^N \frac{\rho_k d_k^3}{1 + \Gamma d_k}$$

$$a_i = \frac{\alpha^2 [z_i - (\pi/(2\Delta)) d_i^2 P_n]}{2\Gamma(1 + \Gamma d_i)}$$

$$M_i = \left(\frac{((2\Gamma a_i)/\alpha^2) - z_i}{d_i} \right)$$

The shielding parameter Γ can be obtained from

$$4\Gamma^2 = \alpha^2 \sum_{k=1}^N \rho_k \left[\frac{z_k - (\pi/2\Delta) d_i^2 P_n}{1 + \Gamma d_k} \right]^2 \quad (17)$$

Eq. (17) can be solved by a simple iterative procedure.

The expression for hard-sphere term was obtained from the equation of state for a mixture of hard spheres [21,22].

$$\ln \gamma_i^{\text{hs}} = -\ln \Delta + \frac{\pi P^{\text{hs}} d_i^3}{6kT} + E + 3F^2 G - F^3 H \quad (18)$$

where

$$E = \frac{3\xi_2 d_i + 3\xi_1 d_i^2}{\Delta} + \frac{9\xi_2^2 d_i^2}{2\Delta^2}$$

$$F = \frac{\xi_2 d_i}{\xi_3}$$

$$G = \ln \Delta + \frac{\xi_3}{\Delta} - \frac{\xi_3^2}{2\Delta^2}$$

$$H = 2\ln \Delta + \frac{\xi_3(2 - \xi_3)}{\Delta}$$

$$P^{\text{hs}} = \frac{6kT}{\pi} \left[\frac{\xi_0}{\Delta} + \frac{3\xi_1 \xi_2}{\Delta^2} + \frac{\xi_2^3(3 - \xi_3)}{\Delta^3} \right]$$

In Eqs. (16)–(18), the anion diameters are kept constant, and their values can be found in [15]. The cation diameter is the effective diameter of a hydrated ion. It can be calculated by [15]

$$d_+ = d_0 - \lambda_1 \frac{I^{1/2}}{1 + I^{1/2}} - \lambda_2 I^2 \quad (19)$$

where d_0 , λ_1 and λ_2 are the effective diameter parameters of the cations, and can be obtained from Lu et al. [15]. For the four electrolyte which were not included in [15], the effective diameter parameters of the cations were regressed in this work from the activity coefficient data taken from [23], and they can be found in Appendix A.

It should be pointed out that the activity coefficient calculated from Eqs. (15)–(19) is based on the molarity scale and in the McMillan–Mayer (MM) reference state. It can be changed into that in the Lewis–Randall (LR) reference state using the equation of Pailthorpe et al. [24].

$$\ln \gamma_{\pm}^{\text{LR}} = \ln \gamma_{\pm}^{\text{MM}} - \frac{\Pi \bar{V}_{\pm}}{RT} \quad (20)$$

where the osmotic pressure is calculated by $\Pi = \nu RT m M_w \phi / 1000 \bar{V}_w$, \bar{V}_{\pm} and \bar{V}_w are the mean partial molar volume of the electrolyte and the partial molar volume of water, respectively. The partial molar volumes of the electrolyte and water can be obtained from the density of the electrolyte solution. In this work, the equation of Novotuy and Sohnel [25] was adopted to express the densities of a single electrolyte solution.

When the activity coefficient was obtained, the osmotic coefficient can be calculated from

$$\phi = 1 + \frac{1}{m} \int_0^m m \, d \ln \gamma_{\pm} \quad (21)$$

The modified MSA can give very accurate osmotic coefficient for the single electrolyte solutions up to high concentration. Fig. 1 gives comparisons of the calculated osmotic coefficient with the smoothed experimental value [26] for LiBr solution at 298.15 K. The results of the modified MSA are in very good agreement with the smoothed experimental osmotic coefficients in the whole concentration range.

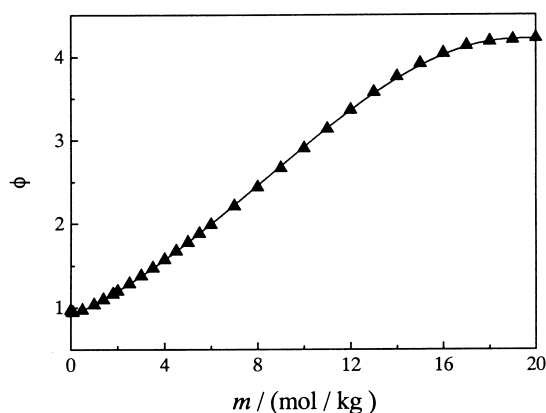


Fig. 1. Comparison of experimental smoothed osmotic coefficients with values calculated from the modified MSA for LiBr at 298.15 K: (▲) experimental value of Hammer and Wu [26]; (—) the modified MSA.

2.5. Surface tension for aqueous mixed electrolyte solution

The expression of surface tension for a single electrolyte solution can be extended to a mixed electrolyte solution as [13]

$$\sigma_m = \sigma_w + \frac{RT}{55.51A_w} \left(\phi_m^B \sum_j v_j m_j^B - \phi_m^S \sum_j g_j v_j m_j^B \right) \quad (22)$$

where $v_j = v_{j+} + v_{j-}$. If the value of g_j is assumed to be affected by the total molality of the electrolytes in aqueous solutions, Eq. (13) can be modified as

$$g_j = 1 - \frac{\beta_j}{1 + 2 \sum v_j m_j^B / 55.51} \quad (23)$$

where β_j is the parameter of electrolyte j .

In this work, a simple approach proposed by Lu et al. [15] was employed to calculate the osmotic coefficients in mixed electrolyte solutions according to the ionic strength fraction y_j

$$\phi_m(I, T) = \sum_j \phi_j(I, T) y_j \quad (24)$$

where $\phi_j(I, T)$ is the osmotic coefficient of the single electrolyte solution at temperature T and ionic strength I . It was calculated from Eq. (21).

When the osmotic coefficients in both surface and bulk liquid phases were obtained from Eq. (24), Eq. (22) along with Eq. (23) can be used to predict surface tensions of the mixed electrolyte solutions.

3. Results and discussion

The method proposed in this work has been applied to 31 single electrolyte aqueous solutions. In the calculation, the dielectric constant of water was obtained from the Malmberg and Maryott equation [27]

$$D = 87.74 - 0.40008t + 9.398 \times 10^{-4}t^2 - 1.41 \times 10^{-6}t^3 \quad (25)$$

where $t = T - 273.15$.

The surface parameter β was determined by fitting the experimental surface tension data of Abramzon and Gauberk [28–30] at only one temperature. The values of β , the average absolute deviations (AAD), the maximum fitting concentration and the temperatures of the solutions are listed in Table 1. The sources of the surface tension data are listed in the last column of the table. From Table 1 one can see that the correlation is quite good with a total AAD of 0.70%, and the parameter β has a good physical meaning. The values of parameter β are negative for strong inorganic acids, and are positive for all salts studied. Unlike inorganic salts, the inorganic acids such as HCl, HNO₃ and HClO₄ have a big vapor pressure and they are volatile substances. They have a trend to escape from the bulk liquid phase through the surface phase, as a result the concentration of the acids in the surface phase is bigger than that in the bulk liquid phase, and a negative value of β is obtained for these inorganic acids. For chlorhydric acid and aqueous alkali chloride solutions, the values of parameter β is in the order

$$H^+ < Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$

Table 1
Surface parameter and AAD in the correlation of the surface tensions for single electrolyte solutions at one temperature

Salt	T (K)	m_{\max}	β	AAD (%)		Reference
				Present	Li et al. [13]	
AgNO ₃	293.15	6.02	0.2482	0.54	1.61	[28]
BaCl ₂	303.15	1.60	0.1843	0.14	1.15	[28]
CaCl ₂	298.15	7.00	0.0791	1.19	2.88	[28]
CsCl	298.15	8.88	0.1718	0.43	0.57	[28]
HCl	293.15	11.07	−0.0086	0.20	0.91	[28]
HClO ₄	298.15	25.92	−0.0050	2.26	2.69	[28]
HNO ₃	293.15	19.08	−0.0566	1.62	0.96	[28]
KBr	293.15	5.60	0.1287	0.43	0.34	[29]
KCl	293.15	4.18	0.1468	0.17	0.09	[29]
KI	298.15	7.28	0.0994	0.55	0.17	[29]
KNO ₃	298.15	2.63	0.1807	0.26	0.14	[29]
KOH	293.15	7.06	0.0945	0.48	1.71	[29]
K ₂ SO ₄	298.15	1.05	0.3997	0.17	0.56	[29]
LaCl ₃	298.15	1.03	0.2418	0.12	0.30	[29]
LiBr	303.15	17.27	0.0417	2.12	4.08	[29]
LiCl	298.15	15.67	0.0636	1.63	3.10	[29]
LiOH	293.15	4.12	0.1330	0.36	0.37	[29]
MgCl ₂	293.15	3.50	0.0591	1.46	1.84	[29]
NaBr	293.15	6.48	0.1095	1.33	1.60	[30]
NaCl	293.15	5.70	0.1219	0.48	0.52	[30]
NaClO ₄	298.15	1.54	0.0522	0.04	0.12	[30]
NaI	298.15	8.82	0.0509	0.68	1.17	[30]
NaNO ₃	303.15	11.77	0.1320	0.58	1.59	[30]
NaOH	293.15	6.25	0.1091	0.29	1.42	[30]
Na ₂ SO ₄	303.15	1.24	0.2905	0.19	1.46	[30]
NH ₄ Cl	298.15	5.62	0.1255	0.16	0.21	[30]
NH ₄ NO ₃	293.15	19.36	0.2474	1.42	0.60	[30]
(NH ₄) ₂ SO ₄	391.15	5.60	0.2211	0.96	1.64	[30]
RbCl	298.15	6.93	0.1501	0.47	0.23	[30]
SrCl ₂	293.15	2.81	0.1294	0.46	0.65	[30]
Sr(NO ₃) ₂	291.15	3.12	0.2277	0.52	1.01	[30]
				0.70 ^a	1.15 ^a	

^a Total average absolute deviation (%).

The molality ratios g for the six chloride solutions are plotted in Fig. 2 against the molality of electrolyte in the bulk liquid phase up to 6 mol/kg. The 1:1 valency chloride adsorbed on the surface phase is dependent on the diameter of the lone cation. The bigger the cation is, the fewer the chloride adsorbed on the surface layer is. The values of β obtained in this work are dependent not only on the cation species but also on the anion species because in present model the cations and anions ionized from an electrolyte are assumed to be adsorbed on the surface phase in the same ratios. This assumption keeps the neutrality of the surface phase. From Fig. 2 one can see that at dilution limit, the ratio g tends to a constant. This is different from the previous study [13], in which it was proposed that g is zero in the case of infinite dilution.

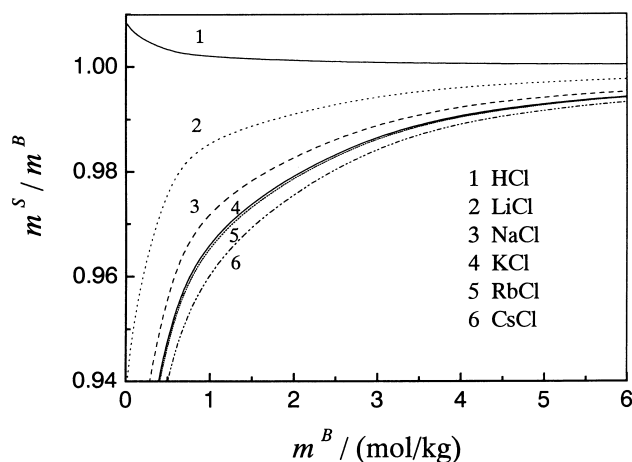


Fig. 2. Concentration ratio between the surface phase and the bulk phase for aqueous HCl and alkali chloride solutions.

For comparison, the AADs obtained from the model of Li et al. [13] are also listed in Table 1. The present model gives better results than that of Li et al. [13] for almost all the electrolyte solutions studied. The present model can be used to correlate surface tension of electrolyte solutions up to saturation. From the calculation, we found that the correlation of Li et al. [13] is not suitable for 1:2 valency systems and the parameter g , which is the molality ratio between surface and bulk liquid phases, has to be set to zero.

Comparisons of the correlated results from two models are made in Fig. 3 for aqueous CaCl_2 solution at 298.15 K. As shown in Fig. 3, both models underestimate the surface tensions at low concentration and overestimate the surface tensions at high concentration, but the present model gives smaller deviations than that of Li et al. [13].

In order to test the dependence of the present model on temperature, the present model has been used to predict the surface tension of single electrolyte solutions at different temperatures by assuming parameter β to be independent on temperature. The predicted results are listed in Tables 2 and 3. All the predicted

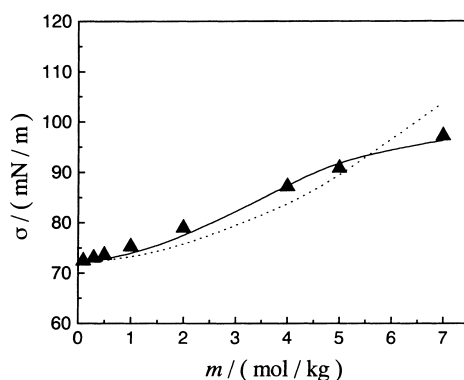


Fig. 3. Comparison of the experimental surface tension vs. the correlated results for aqueous CaCl_2 solution at 298.15 K: (—) this work; (···), calculated values of Li et al. [13]; (▲) experimental values [28].

Table 2

Comparison of predicted results from present work and Li et al. [13] for 1:1 valency electrolyte solutions at different temperatures

T (K)	m_{\max}	AAD (%)		T (K)	m_{\max}	AAD (%)	
		Present	Li et al.			Present	Li et al.
NaCl ^a				NaBr ^a			
298.15	5.49	0.24	0.29	283.15	6.48	1.45	1.95
303.15	5.70	0.87	0.89	303.15	6.48	1.30	1.60
313.15	5.70	1.05	1.13	313.15	6.48	1.34	1.57
323.15	5.70	1.25	1.35	323.15	6.48	1.33	1.55
KCl ^b				333.15	6.48	1.31	1.73
298.15	4.18	0.11	0.43	343.15	6.48	1.28	1.87
303.15	4.18	0.17	0.61	353.15	6.48	1.38	2.06
313.15	5.16	0.52	0.90	NaI ^a			
323.15	5.16	0.62	0.99	293.15	8.81	0.55	1.08
333.15	5.16	1.15	1.36	303.15	8.81	0.84	1.29
343.15	3.35	0.25	0.41	313.15	8.81	1.18	1.53
353.15	3.35	0.20	0.37	323.15	8.81	1.58	1.66
KBr ^b				NaNO ₃ ^a			
283.15	5.60	0.44	0.34	291.15	9.84	1.41	0.51
303.15	5.60	0.45	0.47	293.15	5.04	0.35	0.37
313.15	5.60	0.57	0.66	313.15	11.8	0.86	1.74
323.15	5.60	0.58	0.77	323.15	11.8	1.14	1.74
333.15	5.60	0.47	0.70	333.15	11.8	1.50	2.04
343.15	5.60	0.31	0.53	343.15	11.8	1.28	2.20
353.15	5.60	0.17	0.24	353.15	11.8	1.38	2.28
LiBr ^b				LiCl ^b			
283.15	17.2	2.06	3.50	293.15	15.7	1.92	3.41
293.15	17.2	1.86	3.82	303.15	15.7	2.07	3.68
313.15	17.2	2.45	4.28	313.15	16.7	2.35	4.08
323.15	17.2	2.68	4.52	323.15	16.7	2.50	4.44
333.15	17.2	2.88	4.79	333.15	16.7	2.63	4.67
343.15	17.2	2.98	5.02	CsCl ^c			
353.15	17.2	3.08	5.33	293.15	8.88	0.57	0.86
				303.15	8.88	0.45	0.74
						1.23 ^d	1.89 ^d

^a The experimental surface tension data were taken from [30].

^b The experimental surface tension data were taken from [29].

^c The experimental surface tension data were taken from [28].

^d Total average absolute deviation (%).

results were compared with that of Li et al. [13]. The predicted results are satisfactory for the engineering uses over a range of temperature from 283.15 to 353.15 K.

In Fig. 4 the surface tension of aqueous KCl solution at different temperatures predicted from the present model is compared with the experimental values [29] and with the prediction of Li et al. [13]. As seen in Fig. 4, the present model is in good agreement with the experimental values, while the model of Li et al. [13] underestimates the surface tensions in the moderate concentration region.

Table 3

Comparison of predicted results from present work and Li et al. [13] for 1:2 and 2:1 valency electrolyte solutions at different temperatures

T (K)	m_{\max}	AAD (%)		T (K)	m_{\max}	AAD (%)	
		Present	Li et al.			Present	Li et al.
BaCl_2^{a}				$\text{Na}_2\text{SO}_4^{\text{b}}$			
293.15	1.60	0.20	1.23	293.15	1.24	0.19	1.57
313.15	1.60	0.08	0.77	313.15	1.24	0.22	1.45
323.15	1.60	0.56	0.79	323.15	1.24	0.60	1.86
333.15	1.60	0.22	0.41	333.15	1.24	0.67	2.04
343.15	1.60	0.34	0.23	343.15	1.24	1.05	2.36
353.15	1.60	0.45	0.31	353.15	1.24	1.19	2.69
MgCl_2^{c}				$(\text{NH}_4)_2\text{SO}_4^{\text{b}}$			
313.15	3.50	2.07	2.33	303.15	5.60	0.72	1.36
323.15	3.50	2.50	2.79	313.15	5.07	0.99	1.97
343.15	3.50	2.90	3.33	323.15	5.07	1.23	2.60
				333.15	5.07	1.43	2.83
				343.15	5.07	1.58	2.98
				353.15	5.07	1.65	3.05
						0.99 ^d	1.85 ^d

^a The experimental surface tension data were taken from [28].

^b The experimental surface tension data were taken from [30].

^c The experimental surface tension data were taken from [29].

^d Total average absolute deviation (%).

The present model has been tested for 14 mixed electrolyte aqueous solutions at different temperatures. In the calculation, only the parameters β obtained from relevant single electrolyte solutions were used. The predicted results from the present model along with that of Li et al. [13] are shown in Table 4. The experimental surface tensions for the mixed electrolyte solutions studied were taken from [31]. As seen from Table 4, the present model gives total AAD of 0.63% while the model of Li et al. [13] gives total

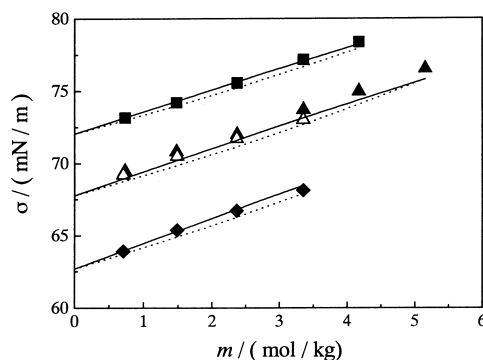


Fig. 4. Comparison of the experimental surface tension vs. the predicted results for aqueous KCl solutions at different temperatures: (—) this work; (· · ·) Li et al. [13]; symbols refer to the experimental values [29]: (■), 298.15 K; (▲) and (△) 323.15 K; (◆) 353.15 K.

Table 4

Comparison of the AAD in the prediction of the surface tension of aqueous mixed electrolyte solutions from present work and Li et al. [13]^a

System	T (K)	I_{\max}	AAD (%)	
			Present	Li et al.
KBr–KCl–H ₂ O	291.15	4.90	0.38	0.40
KNO ₃ –NH ₄ Cl–H ₂ O	291.15	4.84	0.44	0.34
KBr–NaBr–H ₂ O	283.15	6.26	0.88	0.91
	303.15	6.26	1.04	1.24
	323.15	6.26	1.13	1.43
	343.15	6.26	1.19	1.75
	291.15	7.45	0.22	0.95
KBr–Sr(NO ₃) ₂ –H ₂ O	291.15	5.79	0.42	1.38
KNO ₃ –Sr(NO ₃) ₂ –H ₂ O	291.15	7.94	0.19	1.10
NH ₄ Cl–Sr(NO ₃) ₂ –H ₂ O	291.15	9.60	0.62	2.49
NaNO ₃ –Sr(NO ₃) ₂ –H ₂ O	291.15	11.2	0.39	1.35
NH ₄ Cl–(NH ₄) ₂ SO ₄ –H ₂ O	291.15	13.4	0.87	2.13
NaNO ₃ –(NH ₄) ₂ SO ₄ –H ₂ O	291.15	5.55	0.78	0.37
KBr–KCl–NH ₄ Cl–H ₂ O	291.15	5.70	0.61	0.75
KBr–KNO ₃ –Sr(NO ₃) ₂ –H ₂ O	291.15	7.18	0.42	0.47
KBr–NH ₄ Cl–Sr(NO ₃) ₂ –H ₂ O	291.15	6.13	0.49	0.49
KNO ₃ –NH ₄ Cl–Sr(NO ₃) ₂ –H ₂ O	291.15	10.8	0.56	0.79
NH ₄ Cl–NaNO ₃ –(NH ₄) ₂ SO ₄ –H ₂ O	291.15		0.63 ^b	1.08 ^b

^a The experimental surface tension data were taken from [31].

^b Total average absolute deviation (%).

AAD of 1.08%. The two models give almost the same AAD for the symmetrically mixed electrolyte solutions.

Fig. 5 shows the comparisons of experimental surface tensions of aqueous NH₄Cl–Sr(NO₃)₂ solution with values predicted from Li et al. [13] and the present model. Fig. 6 is the same kind of comparison plots of surface tensions as a function of the ionic strength for aqueous NaNO₃–(NH₄)₂SO₄ solution. In

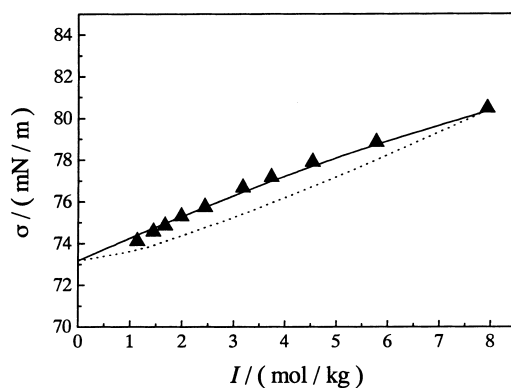


Fig. 5. Comparison of the experimental surface tensions vs. the predicted results for aqueous NH₄Cl(1)–Sr(NO₃)₂(2) solution ($\gamma_1=0.486$) at 291.15 K: (—) this work; (···) Li et al. [13]; (▲) experimental values [31].

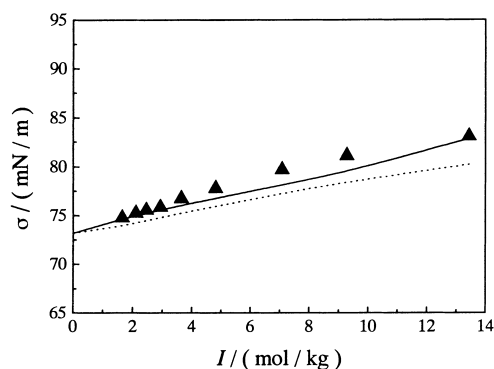


Fig. 6. Comparison of the experimental surface tensions vs. the predicted results for aqueous $\text{NaNO}_3(1)-(\text{NH}_4)_2\text{SO}_4(2)$ solution ($v_1=0.357$) at 291.15 K: (—) this work; (···) Li et al. [13]; (▲) experimental values [31].

both cases, the present model gives excellent prediction for the surface tensions over entire ionic strength range. The model of Li et al. [13] underestimates the surface tensions of the mixed electrolyte solutions as this type.

4. Conclusion

Based on the assumption that the surface layer can be treated as a separate phase between the vapor and bulk liquid phases, the surface tensions of concentrated single and mixed electrolyte aqueous solutions are correlated and predicted using the modified MSA and the Rasmussen area of water. The molality ratio between surface and bulk liquid phases are expressed as a function of the concentration of electrolyte in the bulk liquid phase. The values of the surface parameter β for 31 single electrolyte solutions are obtained at one temperature. By using the obtained parameter β , surface tensions of single and mixed electrolyte solutions at different temperatures (283.15–353.15 K) can be predicted with good accuracy. The comparisons between the present model and that of Li et al. [13] are carried out, and the calculated result shows that the present model is superior in the prediction of the surface tensions for the electrolyte solutions studied.

List of symbols

A	molar surface area (cm^2/mol)
\bar{A}	partial molar surface area (cm^2/mol)
AAD	average absolute deviation (%)
a	activity
D	dielectric constant of pure water
d	diameter of ion (nm)
d_0	effective diameter parameters of the cations (nm)
e	unit electronic charge (C)
g	molality ratio between surface and bulk liquid phases
I	ionic strength (mol/kg)

k	Boltzmann constant
M	molecular weight (g/mol)
m	molality concentration (mol/kg)
N	number of ion
P	pressure (Pa)
R	gas constant (8.3144J/(mol K))
T	absolute temperature (K)
\bar{V}	partial molar volume (cm ³ /mol)
y	ion strength fraction
z	valence of ion

Greek letters

Π	osmotic pressure (Pa)
β	surface parameter in Eqs. (13) and (23)
γ	activity coefficient
ν	stoichiometric coefficient
ρ	number density (nm ⁻³)
$\sigma, \sigma_m, \sigma_w$	surface tensions of electrolyte solutions and water (mN/m)
λ_1, λ_2	effective diameter parameters of the cations
ϕ	osmotic coefficient
μ	chemical potential (J/mol)

Superscripts

B	bulk liquid phase
elec	electrostatic
hs	hard sphere
LR	Lewis–Randall reference state
MM	McMillan–Mayer reference state
S	surface phase
0	standard state

Subscripts

i, k	ions i and k
j	electrolyte j
m	mixed electrolyte solution
w	water
\pm	ion average
+	cation
–	anion

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 29736170) and part financial support was from the State Key Laboratory of Chemical Engineering in China.

Table 5

The effective diameter parameters of the cations and the relative deviations in γ_{\pm} calculated from the modified MSA for the four electrolytes which were not included in [15]^a

Salt	Parameters (nm)			m_{\max}	AAD (%)
	$\sigma_0 \times 10$	$\lambda_1 \times 10$	$\lambda_2 \times 10^4$		
AgNO ₃	7.610	4.512	−0.687	6.0	0.17
LiOH	0.963	–	–	4.0	1.15
(NH ₄) ₂ SO ₄	3.862	1.370	−1.370	4.0	0.51
Sr(NO ₃) ₂	7.610	4.512	−0.687	4.0	0.60

^a $T=298.15$ K.

Appendix A

For the electrolytes AgNO₃, LiOH, (NH₄)₂SO₄ and Sr(NO₃)₂, the effective diameter parameters of cations for the modified MSA were not included in [15], They were regressed from the experimental activity coefficient data [23] and are listed in Table 5. The maximum concentration of fitting along with the average absolute deviation of γ_{\pm} are also included in Table 5.

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