Prediction of Surface Tension in Single and Mixed Electrolyte Solutions

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Abstract

In this study, the Langmuir adsorption isotherm has been coupled with activity coefficient models for prediction of surface tension of single and mixed electrolyte solutions. Various activity models such as Meissner, Pitzer and extended UNIQUAC have been used and coupled with Langmuir adsorption isotherm. The model parameters were determined through mathematical optimization using experimental surface tension data of single electrolyte solutions. Absolute average deviation was used as objective function in optimization procedure. The results showed that in the case of single electrolyte solutions different activity coefficient models have similar capability while in the case of mixed electrolyte solutions, extended UNIQUAC model gives better results.

Keywords: *Surface Tension, Langmuir, Extended UNIQUAC, Pitzer, Meissner*

1. Introduction

Knowledge about the surface tension of electrolyte solution is essential in chemical engineering processes such as liquid-liquid extraction, emulsification, demulsification and various separation methods. As an example, surface tension is effective in the fluid flow through porous media [1]. In addition, variation of surface tension can significantly affect the mass transfer rate in distillation columns [2, 3]. There are simple methods for calculation of surface tension of pure liquids while prediction of surface tension of mixtures is really difficult, especially for electrolyte solutions. Many processes deal with the mixed electrolyte solutions such as mineral industries, in this regard knowledge about surface tension of mixed electrolyte solution will be useful.

In recent years different methods have been presented for calculation of surface tension of mixtures [4-11]. Using the equality of the chemical potential in the bulk and surface of liquid is one of the most applicable methods. For this purpose the activity of the solvent or osmotic coefficient should be known. Yu *et al.* [4] used the modified mean spherical approximation model for calculation of

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solvent activity and showed that it gives a fairly accurate result for single electrolyte solutions up to high concentration. Li *et al.* [5] used Pitzer equation for calculation of osmotic coefficient. Their model could predict the surface tension of single and also mixed electrolyte solutions at different temperature. The interface parameters were evaluated from correlating the surface tension data of single electrolyte aqueous solutions at one temperature. Hu *et al.* [6] utilized Patwardhan and Kumar's equation for calculation of water activity in mixed electrolyte solutions. They compared their results with Li *et al.*'s work. Hu [7] presented a new simple predictive equation for multi-component solutions, they used a linear isopiestic relation based on Butler equations. Experimental data on binary subsystems is essential for this model. In a different approach, the Gibbs adsorption equation has been used [8-10] for prediction of surface tension of mixtures. Our literature review showed that this approach is more applicable for prediction of surface tension of mixture as well as mixed electrolyte solutions [8-10]. Desnoyer *et al.* [8] utilized this concept for prediction of interfacial tension between a mixture of organic solvent and aqueous electrolyte solutions based on Gibbs and Langmuir adsorption equation. Li and Lu [9, 10] modified Desnoyer *et al.* model through employing the Meissner and Pitzer activity models. This method was successfully applied for calculation of surface tension and interfacial tension of mixed aqueous electrolyte solutions. They claimed that in their proposed model, the activity coefficient model has determinant effect in accurate prediction of surface tension and interfacial tension. In a different approach artificial neural network has been used for prediction of surface tension in binary mixtures [11].

In most of the previous works, surface tension of single electrolyte solution has been correlated using one or two adjustable parameters. In this work the capability of different activity models in prediction of surface tension of mixed electrolyte solution has been investigated.

2. Theory
2-1. Surface tension model for single electrolyte solutions

In the aqueous electrolyte solution, between vapor and liquid at the constant temperature and pressure, the Gibbs adsorption equation states that [12]:

$$-d\sigma_{Int} = \Gamma_w d\mu_w^{Int} + \sum_{all\ salts} \Gamma_{ij} d\mu_{ij}^{Int} \qquad (1)$$

where σ_{Int} is equilibrium surface tension, Γ_w, Γ_{ij}, μ_w^{Int} and μ_{ij}^{Int} represent the interfacial excess and chemical potentials of water and the electrolyte *ij*, respectively. For an aqueous solution including a single electrolyte, Eq. (1) reduces to:

$$-d\sigma_{Int} = \Gamma_w d\mu_w^{Int} + \Gamma_{\pm} d\mu_{\pm}^{Int} \qquad (2)$$

where, Γ_w and $\Gamma_{\pm}$ are defined relative to an arbitrarily chosen dividing surface. In order to simplify the equation (2), it is feasible to locate the arbitrary surface so that $\Gamma_w = 0$. In this condition Eq. (2) will shrink to the following form:

$$-d\sigma_{Int} = \Gamma_{\pm}^w d\ln\mu_{\pm} \qquad (3)$$

In an electrolyte solution, salt chemical potential can be defined as follows:

$$\mu_{\pm} = v_{+}\mu_{+} + v_{-}\mu_{-} \tag{4}$$

Where, in the molality scale framework we will have:

$$\mu_{\pm} = \mu_{\pm}^{0} + v_{+}RT\ln(m_{+}\gamma_{+}) + v_{-}RT\ln(m_{-}\gamma_{-}) \tag{5}$$

$$\mu_{\pm} = \mu_{\pm}^{0} + RT\ln\left(m_{+}^{v^{+}}m_{-}^{v^{-}}\right) + RT\ln\left(\gamma_{+}^{v^{+}}\gamma_{-}^{v^{-}}\right)$$
$$= \mu_{\pm}^{0} + RT\ln\left(a_{+}^{v^{+}}a_{-}^{v^{-}}\right) \tag{6}$$

Where, $\mu_{\pm}^{0} = v_{+}\mu_{+}^{0} + v_{-}\mu_{-}^{0}$. After rearrangement, the following relation will be obtained:

$$\mu_{\pm} = \mu_{\pm}^{0} + vRT\ln(m_{\pm}\gamma_{\pm}) = \mu_{\pm}^{0} + RT\ln\left(a_{\pm}^{v}\right) \tag{7}$$

Where $v = v_{+} + v_{-}$, $a_{\pm}$, $m_{\pm}$ and $\gamma_{\pm}$ are the molality scale mean ionic activity, the mean ionic molality and mean ionic activity coefficient respectively. If the salt chemical potential is substituted in Eq. (3), the following equation will be obtained:

$$-d\sigma_{Int} = RT\,\Gamma_{\pm}^{w}d\ln a_{\pm}^{v} \tag{8}$$

Li and Lu [9, 10] assumed that $a_{\pm}^{v} = a_{s}$, consequently, salt activity can be calculated using $a_{s} = a_{\pm}^{v} = \left[v_{+}^{v^{+}}v_{-}^{v^{-}}\left(\gamma_{\pm}m_{\pm}\right)^{v}\right]$. By using Langmuir [13], at equilibrium condition, the rate of adsorption and desorption of the electrolyte on surface must be equal:

$$k_{a_{\pm}}\left(1-\theta_{\pm}\right)a_{s} = k_{d_{\pm}}\theta_{\pm} \tag{9}$$

where $\theta_{\pm}$ is the occupied interface fraction by the electrolyte and $k_{a_{\pm}}$ and $k_{d_{\pm}}$ refer to the adsorption and the desorption constant rate respectively. Rearranging Eq. (9) leads us to Eq. (10):

$$\theta_{\pm} = \frac{K_{\pm}a_{s}}{1+K_{\pm}a_{s}} \tag{10}$$

$K_{\pm} = k_{a_{\pm}}/k_{d_{\pm}}$ is defined as the adsorption equilibrium constant. On the other hand, by assuming mono layer adsorption of electrolyte at the interface[13], the occupied interface fraction by electrolyte is defined as:

$$\theta_{\pm} = \frac{n_{\pm}^{Int}}{n_{\pm}^{Int\,\infty}} \tag{11}$$

Here $n_{\pm}^{Int}$, $n_{\pm}^{Int\infty}$ indicate the number of moles and the maximum number of electrolytes at the interface. By dividing the numerator and the denominator of Eq. (11) by A^{Int} (the interfacial area) we will have:

$$\theta_{\pm} = \frac{n_{\pm}^{Int}/A^{Int}}{n_{\pm}^{Int\infty}/A^{Int}} = \frac{\Gamma_{\pm}}{\Gamma_{\pm}^{\infty}} \tag{12}$$

In Eq. (12), $\Gamma_{\pm}$ and $\Gamma_{\pm}^{\infty}$ refer to the interfacial excess of electrolyte and the maximum interfacial excess. The Gibbs dividing interface with $\Gamma_{w} = 0$ yields:

$$\theta_{\pm} = \frac{\Gamma_{\pm}^{w}}{\Gamma_{\pm}^{w\,\infty}} \tag{13}$$

In which $\Gamma_{\pm}^{w}$ and $\Gamma_{\pm}^{w\infty}$ indicate the interfacial excess and the maximum interface excess respectively when $\Gamma_w = 0$. Combining Eq. (10) and Eq. (13) leads to the following form:

$$\Gamma_{\pm}^{w} = \Gamma_{\pm}^{w\infty} \frac{K_{\pm}a_s}{1+K_{\pm}a_s} \tag{14}$$

Substituting Eq. (14) into Eq. (8) yields:

$$-d\,\sigma_{Int} = \Gamma_{\pm}^{w\infty} \frac{K_{\pm}a_s}{1+K_{\pm}a_s} RTd\,\ln a_s \tag{15}$$

Integrating Eq. (15) from $a_s = 0$ to a_s leads to the following equation for estimating surface tension of aqueous single electrolyte solutions:

$$\sigma_{Int} = \sigma_{Int\,0} + RT\,\Gamma_{\pm}^{w\infty} \ln \frac{1}{1+K_{\pm}a_s} \tag{16}$$

In Eq. (16), σ_{Int0} is the surface tension of pure water in absence of any electrolyte at the system temperature. $\Gamma_{\pm}^{w\infty}$ and $K_{\pm}$ are the model parameters which are determined by minimizing the following objective function:

$$f = \left(100/_n\right) \left[\frac{|\gamma_{calc} - \gamma_{exp}|}{\gamma_{exp}} \right] \tag{17}$$

2-2. Surface tension model for mixed electrolyte solutions

Prediction of surface tension of mixed electrolyte solutions can be made by two different models. Li and his coworker [9, 10] presented two models for non-competing (Model 1) and competing (Model 2) adsorption of electrolytes:

Model 1:

$$\sigma_{Int} = \sigma_{Int\,0} + \sum RT\,\Gamma_{\pm}^{w\infty} \ln \frac{1}{1+K_{\pm}a_s} \tag{18}$$

Model 2:

$$\sigma_{Int} = \sigma_{Int\,0} + RT \sum \Gamma_{\pm}^{w\infty} \ln \left(1 - \frac{K_{\pm}a_s}{1+\sum K_{\pm}a_s} \right) \tag{19}$$

In the above equations, adjustable parameters ($K_{\pm}$, $\Gamma_{\pm}^{w\infty}$) as well as electrolyte mean ionic activity (a_s) must be known for calculation of surface tension. Usually, adjustable parameters are determined using experimental data on surface tension of single electrolyte solution. The adjusted parameters can then be used for mixed electrolyte solutions. The accuracy of the model depends on the accuracy of electrolyte activity in the mixed electrolyte solutions. In the previous works Meissner as well as Pitzer activity models have been utilized [9, 10]. In order to achieve a general judgment about the capability of various activity models, in this work the ability of the extended UNIQUAC model has been compared with Meissner and Pitzer models.

Extended UNIQUAC model was first presented by Sander and co-workers [14]. Later it was modified by Nicolaisen *et al.* [15] as well as Thomsen *et al.* [16]. In this work the last version has been utilized. The available model parameters in the literature have been used in this work [17-20]. Meissner method is an empirical model which includes a graphical method for computing water activities and a technique

for calculating mean ionic activity coefficients in multi-ion solutions. These graphs are based on the reduced activity coefficient versus the ionic strength, for different salts [21-23]. The Pitzer model is an extension of the Debye-Huckel model. In the Pitzer model binary and ternary short-range interactions have been considered using a virial expansion. This model is the most popular model among different theories for electrolyte solutions. Also, these equations can be applied in iterative calculations because the ion interaction parameters are stated as explicit functions of ionic strength and require very few parameters to calculate properties of both single and mixed electrolyte solutions [24]. In this work the activity coefficient of mixed electrolyte solutions is calculated utilizing simplified Pitzer model [25, 26].

3. Results and discussion

In order to check the ability of activity coefficient models in calculation of surface tension, in the first step adjustable parameters using experimental data on single electrolyte solution have been determined. In the case of the Pitzer model, it is found that the dependency of the parameters to the temperature cannot be ignored, because of considerable error observed in prediction of surface tension. However, for small value of activities the observed error was negligible [9]. In Table 1, the model parameters as well as absolute average deviation (AADs %) of three activity coefficient models have been introduced. In the case of single electrolyte solution it can be seen that using the extended UNIQUAC model yields overall

AAD % of 0.27. However, in the case of Pitzer and Meissner models, the overall AADs % are 0.26 and 0.27 respectively. The results show that in this case all models have similar performance. In Figs 1, 2 and 3 the experimental values of surface tensions of $SrCl_2$, HNO_3 and KCl aqueous solutions have been depicted in comparison with the modeling results. In Table 2, the ability of different activity models has been investigated in prediction of surface tension at different temperature. Table 2 indicates that all models can predict surface tension at different temperatures with acceptable accuracy. Considering the above results, it can be concluded that in the case of single electrolyte solutions, all models have similar ability with regard to surface tension. These results can be referred to utilizing two adjustable parameters which have been included in the Gibbs adsorption model. In order to better judge the ability of the various activity models, adjusted parameters were used to predict the surface tension of mixed electrolyte solutions, without using any additional parameter. In Table 3, the results of prediction of surface tension of mixed electrolyte solutions using three activity coefficient models have been reported. Two different adsorption models (Eqs. 18 and 19) have been utilized for this purpose. In the case of first adsorption model, the results showed that the extended UNIQUAC model gives more accurate results, the overall AAD % in prediction of mixed electrolyte surface tension was 1.49, 6.66 and 4.14 achieved by the extended UNIQUAC, Pitzer and Meissner model, respectively. In the case of second adsorption model, the overall AAD %

of 1.83, 3.93 and 3.03 have been obtained using extended UNIQUAC, Pitzer and Meissner models, respectively.

Table 1. The model parameters for Surface Tension of single electrolyte solutions with three models.

Salt	T(K)	m_{Max}	N	$\Gamma_{ca}^{w\infty}$	K	AAD %	$\Gamma_{ca}^{w\infty}$	K	AAD %	$\Gamma_{ca}^{w\infty}$	K	AAD %
				Extended UNIQUAC			*Pitzer*			*Meissner*		
NaNO$_3$[27]	291.15	9.84	10	-1.60e-6	1.23	0.18	-1.59e-6	1.07	0.21	-1.51e-6	1.22	0.20
HNO$_3$[27]	303.15	29.09	10	5.89e-7	0.12	0.61	8.04e-7	0.11	0.90	4.91e-7	0.11	0.76
KNO$_3$[28]	298.15	1.80	6	-1.64e-6	3.33	0.15	-1.64e-6	3.53	0.15	-1.60e-6	3.79	0.15
NH$_4$NO$_3$[28]	298.15	1.90	6	-4.40e-7	5.43	0.18	-4.30e-7	5.57	0.18	-4.53e-7	5.86	0.18
KOH[27]	293.15	3.80	5	-1.09e-6	0.77	0.30	-1.05e-6	0.74	0.30	-1.00e-6	0.68	0.30
NH$_4$Cl[27]	292.15	6.77	11	-7.87e-7	2.17	0.10	-8.71e-7	1.55	0.09	-8.56e-7	1.63	0.08
HCl[27]	293.15	14.98	7	4.84e-7	0.01	0.51	3.43e-7	0.02	0.52	3.02e-7	0.02	0.53
NaCl[29]	298.15	1.00	9	-3.26e-7	15.26	0.05	-3.09e-7	14.96	0.05	-3.06e-7	16.15	0.05
KCl[30]	293.15	1.84	6	-8.14e-7	6.37	0.18	-8.41e-7	5.65	0.19	-8.18e-7	6.10	0.19
MgCl$_2$[31]	298.15	0.81	10	-2.19e-7	609.77	0.11	-2.03e-7	402.57	0.13	-1.78e-7	559.14	0.13
BaCl$_2$[27]	283.15	1.57	4	-2.94e-7	342.50	0.09	-3.48e-7	138.65	0.10	-3.60e-7	192.38	0.10
CaCl$_2$[27]	298.15	7.00	9	-5.53e-7	27.90	0.93	-5.12e-7	24.87	0.43	-5.51e-7	13.60	0.77
SrCl$_2$[27]	293.15	2.82	9	-3.99e-7	756.97	0.18	-4.03e-7	56.35	0.21	-3.99e-7	54.34	0.25
MnCl$_2$[27]	291.15	3.40	6	-6.50e-7	19.53	0.81	-7.19e-7	12.09	0.71	-7.18e-7	21.74	0.69
(NH$_4$)$_2$SO$_4$[32]	290.65	1.00	9	-3.60e-7	208.68	0.09	-3.14e-7	14.19	0.09	-4.41e-7	17.12	0.08
Na$_2$CO$_3$[33]	303.15	0.47	10	-2.13e-7	1035.5	0.05	-1.97e-7	1074.6	0.05	-1.81e-7	1420.5	0.05
Na$_2$SO$_4$[33]	308.15	0.90	11	-3.24e-7	268.44	0.08	-3.14e-7	312.11	0.08	-2.80e-7	389.28	0.08
Overall AAD %						**0.27**			**0.26**			**0.27**
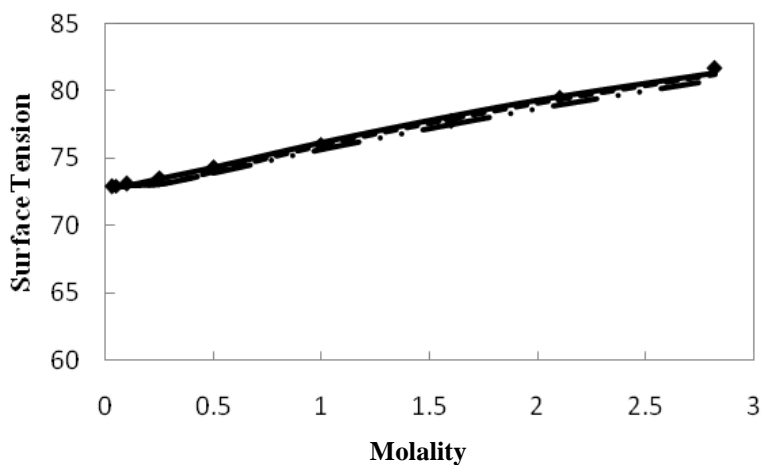
Figure 1. Comparison between calculated and experimental data (♦) of surface tension of SrCl$_2$ versus molality at 293.15. Langmuir&E.UNIQUAC (——), Langmuir&Meissner (-----), Langmuir&Pitzer (— ·—).
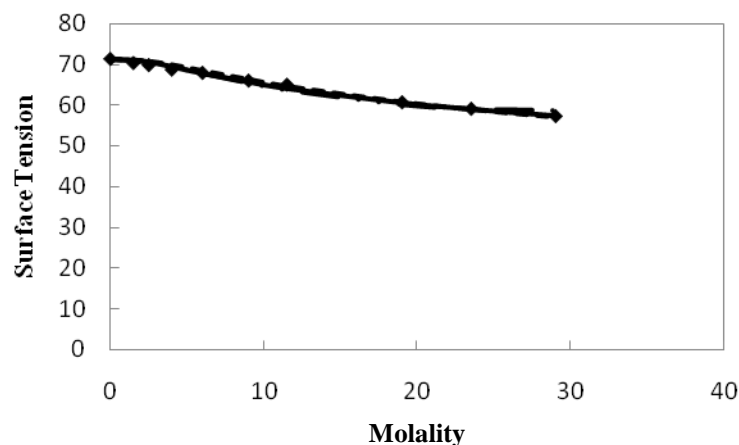
Figure 2. Comparison between calculated and experimental data (♦) of surface tension of HNO_3 versus molality at 303.15. Langmuir&E.UNIQUAC (——), Langmuir&Meissner (-----), Langmuir&Pitzer (— —).
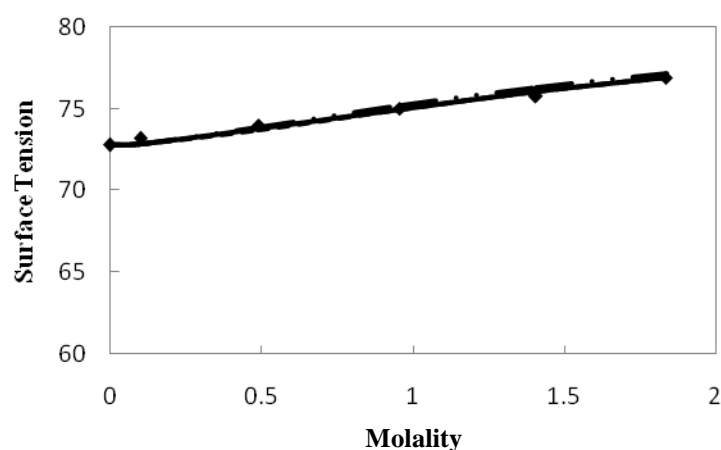
Figure 3. Comparison between calculated and experimental data (♦) of surface tension of KCl versus molality at 293.15.by Langmuir&E.UNIQUAC (——), Langmuir&Meissner (-----), Langmuir&Pitzer (— ·—).

Table 2. Predicted Surface Tension at other temperatures with the same parameters by three models.

Salt	T(K)	m_{max}	N	Extended UNIQUAC	Pitzer	Meissner
NH_4NO_3[28]	303.15, 298.15, 288.15, 283.15,	1.90	6	0.19	0.26	0.19
KNO_3[28]	303.15, 293.15, 288.15, 283.15	1.80	6	0.24	0.20	0.24
$NaCl$[29]	308.15, 303.15, 298.15, 288.15	1.00	9	0.08	0.10	0.09
KCl[30]	303.15, 298.15, 288.15, 283.15	1.84	5	0.60	0.67	0.59
$(NH_4)_2SO_4$[32]	308.15, 305.65, 303.15, 300.65, 298.15, 295.65, 290.65, 288.15	1.00	8	0.10	0.12	0.09
Na_2CO_3[33]	308.15, 298.15, 293.15, 288.15	0.47	10	0.07	0.11	0.08
Na_2SO_4[33]	303.15, 298.15, 293.15, 288.15	0.90	11	0.12	0.17	0.11
Overall AAD %				**0.20**	**0.23**	**0.20**

Table 3. Prediction of Surface Tension in mixed electrolyte solutions by three models.

Salt	T(K)	N	I_{max}	Extended UNIQUAC		Pitzer		Meissner	
				AAD 1%	AAD 2%	AAD 1%	AAD 2%	AAD 1%	AAD 2%
$BaCl_2$ -HCl[27]	298.15	3	3.49	0.27	0.27	6.10	6.10	0.75	0.75
$SrCl_2$ -HCl[27]	298.15	4	5.86	0.72	0.72	6.49	6.49	0.48	0.48
$CaCl_2$ -HCl[27]	298.15	4	4.54	1.20	1.20	7.75	7.75	1.16	1.16
KNO_3-HNO_3[27]	303.15	9	28.99	1.59	0.78	8.64	5.63	26.07	12.17
KNO_3 -NH_4NO_3[27]	298.15	12	2.79	4.90	5.37	6.89	6.05	4.74	5.30
KNO_3-NH_4Cl[27]	291.15	10	4.84	1.81	0.49	10.56	1.27	0.58	0.79
NH_4Cl-$(NH4)_2SO_4$[27]	291.15	10	11.18	1.12	3.49	7.68	1.94	2.73	3.80
$(NH_4)_2SO_4$ -$NaNO_3$[27]	291.15	9	11.46	1.94	4.22	9.97	3.08	3.53	4.05
$NaCl$ -Na_2SO_4[33]	298.15	11	0.83	1.03	1.06	0.46	0.45	1.00	1.04
$NaCl$ -$MgCl_2$[34]	298.15	9	2.00	0.28	0.68	2.06	0.54	0.33	0.75
Overall AAD %				**1.49**	**1.83**	**6.66**	**3.93**	**4.14**	**3.03**

Results have been presented in Table 3. It can be concluded that the extended UNIQUAC model has higher accuracy in prediction of surface tension of mixtures in comparison with the others. This conclusion is more obvious in the Figs. 4 and 5. The results indicated that the extended UNIQUAC model can be used for prediction of surface tension in mixed electrolyte solution efficiently. This is due to the ability of extended UNIQUAC model in prediction of activity coefficient of electrolytes in the mixture. As it is shown in Table 3, the accuracy of Meissner model in prediction of surface tension of KNO_3- HNO_3 system is relatively lower compared to the other models. The results presented in Table 3 show that Meissner activity coefficient model gives acceptable result at low ionic strength while at higher concentration the error will reach up to 12 percent. It seems that the accuracy of Meissner model is dependent on acid concentration. For Meissner and Pitzer models, the second adsorption model has higher accuracy than the first one, however, it is vice versa for extended UNIQUAC model. On the other hand, the overall AAD % of extended UNIQUAC model for both

adsorption models is lower than Meissner and Pitzer models. So, the effect of adsorption model in prediction of surface tension of mixed electrolyte solutions is lower than the accuracy of activity coefficient model.

4. Conclusions

A modified model has been proposed based on the Gibbs and Langmuir adsorption models for prediction of surface tension in mixed electrolyte solutions. Three activity coefficient models including extended UNIQUAC model, Pitzer equation and Meissner method have been utilized for this purpose. The model parameters were estimated using mathematical optimizing and based on single electrolyte experimental data. The modified model (extended UNIQUAC model+ Langmuir adsorption model) can correlate surface tension of single electrolytes

with overall absolute average deviation of 0.27%. Also, overall absolute average deviation of Pitzer equation and Meissner method were 0.26% for 0.27%, respectively. The mentioned results showed that in the case of single electrolyte solution, tested activity coefficient models have similar performances in correlation of single electrolyte data while in prediction of mixed electrolyte surface tension, the results showed that Extended UNIQUAC model is more capable in comparison with Pitzer and Meissner models. These results can be due to the capability of extended UNIQUAC model in prediction of accurate activity coefficient in mixed electrolyte solutions. Finally, it can be concluded that the accuracy of activity model is very important in accurate prediction of surface tension in mixed electrolyte solution.
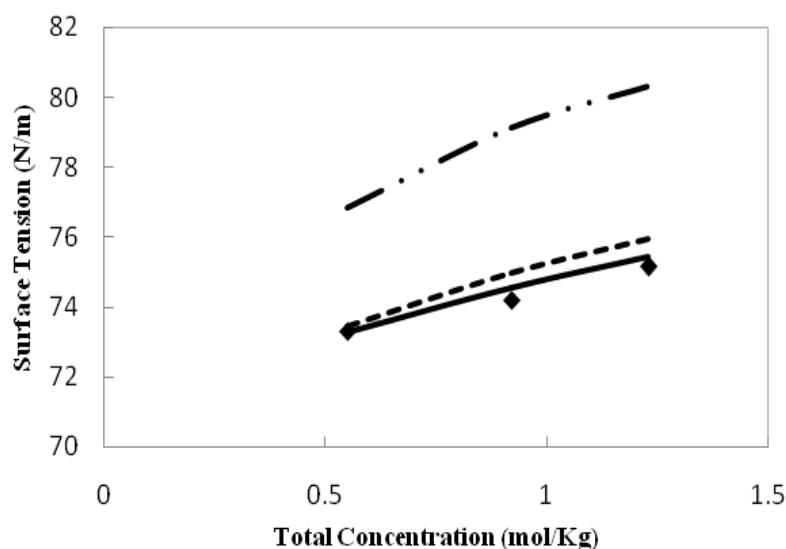
Figure 4. Comparison between calculated and experimental data (♦) of surface tension of $BaCl_2$-HCl versus total molality at 298.15. Langmuir&E.UNIQUAC (——), Langmuir&Meissner (-----), Langmuir&Pitzer (— ·—).
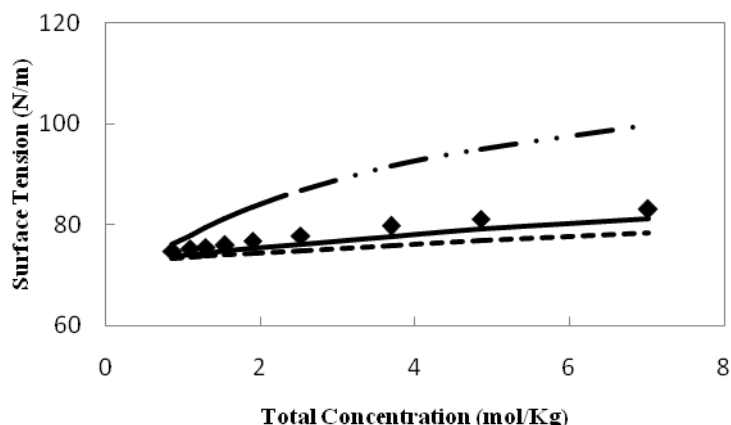
Figure 5. Comparison between calculated and experimental data (♦) of surface tension of $(NH_4)2SO_4$ -$NaNO_3$ versus total molality at 291.15. Langmuir&E.UNIQUAC (——), Langmuir&Meissner (-----), Langmuir&Pitzer (— ·—).

Nomenclature

A^{Int}	interfacial area (m²)
$a_{\pm}$	activity of the electrolyte (cation-anion)
a_+	activity of cation
a_-	activity of anion
$K_{\pm}$	adsorption equilibrium constant
$k_{a_{\pm}}$	adsorption rate constant
$k_{d_{\pm}}$	desorption rate constant
$m_{\pm}$	mean ionic molality (mol/Kg)
m_-	molality of anion (mol/Kg)
m_+	molality of cation (mol/Kg)
$n_{\pm}^{Int}$	number of moles of electrolyte at the interface
$n_{\pm}^{Int\infty}$	maximum number of moles of electrolyte at the interface
R	gas constant (cm³ kPa mol⁻¹K⁻¹)
T	temperature (K)

Greek Symbol

$\gamma_{\pm}$	mean ionic activity coefficient
γ_-	activity coefficient of anion
γ_+	activity coefficient of cation

$\Gamma_{\pm}$	interfacial excess electrolyte (cation- anion)
$\Gamma_{\pm}^{\infty}$	maximum interfacial excess of electrolyte (cation- anion)
Γ_w	interfacial excess of water
Γ_{ij}	interfacial excess of electrolyte ij
$\Gamma_{\pm}^{w}$	interfacial excess of electrolyte by $\Gamma_w= 0$
$\Gamma_{\pm}^{w\infty}$	maximum interface excess of electrolyte by $\Gamma_w= 0$
$\theta_{\pm}$	fraction of interface occupied by the electrolyte
$\mu_{\pm}$	chemical potentials of electrolyte
μ_-	chemical potentials of anion
μ_+	chemical potentials of cation
$\mu_{\pm}^0$	standard mean ionic chemical potentials
μ_-^0	standard chemical potentials of anion
μ_+^0	standard chemical potentials of cation
v_-	stoichiometric coefficient of anion
v_+	stoichiometric coefficient of cation

μ_{ij}^{Int}	chemical potentials of electrolyte ij at interface
μ_{w}^{Int}	chemical potentials of water at interface
$\mu_{\pm}^{Int}$	chemical potentials of electrolyte (cation- anion) at interface
σ_{Int}	equilibrium interfacial tension (mN/m)
σ_{Int}^{0}	equilibrium interfacial tension in absent of electrolyte (mN/m)

References

[1] De Nevers, N., Fluid mechanics for chemical engineers, 2nd ed., McGraw Hill, New York, (1991).

[2] Eckert, C.A. and Prausnitz, J.M., "Statistical surface thermodynamics of simple liquid mixtures", AIChE J., 10, 677, (1964).

[3] Zuiderweg, F.J. and Harmens, A., "The influence of surface phenomena on the performance of distillation columns", Chem. Eng. Sci., 9, 89, (1958).

[4] Yu, Y.X., Gao, G.H. and Li, Y.G., "Surface tension for aqueous electrolyte solutions by the modified mean spherical approximation", J. Fluid Phase Equilib., 173, 23, (2000).

[5] Li, Z.B., Li, Y.G. and Lu, J.F., "Surface tension model for concentrated electrolyte aqueous solutions by the Pitzer equation", Ind. Eng. Chem. Res., 38, 1133, (1999).

[6] Hu, Y.F. and Lee, H., "Prediction of the surface tension of mixed electrolyte solutions based on the equation of Patwardhan and Kumar and the fundamental Butler equations", J. Colloid Interf. Sci., 269, 442, (2004).

[7] Hu, Y.F., "A new predictive equation for the surface tensions of aqueous mixed ionic solutions conforming to the linear isopiestic relation", J. Solution Chem., 32, 897, (2003).

[8] Desnoyer, C., Masbernat, O. and Gourdon, C., "Predictive model for the calculation of interfacial tension in nonideal electrolytic systems", J. Colloid Interf. Sci., 191, 22, (1997).

[9] Li, Z. and Lu, B.C.Y., "Surface tension of aqueous electrolyte solutions at high concentrations- representation and prediction", Chem. Eng. Sci., 56, 2879, (2001).

[10] Li, Z. and Lu, B.C.Y., "Prediction of interfacial tension between an organic solvent and aqueous solutions of mixed-electrolytes", J. Fluid Phase Equilib., 200, 239, (2002).

[11] Parhizgar, H., Dehghani, M.R., Khazaei, A. and Dalirian, M., "Modelling of vaporization enthalpies of petroleum fractions and pure hydrocarbons using genetic program-ming", Ind. Eng. Chem. Res., 51, 2775, (2012).

[12] Adamson, A.W. and Gast, A.P., Physical chemistry of surfaces, 6th ed., Wiley & Sons Inc., New York, (1997).

[13] Langmuir, I., "The adsorption of gases on plane surfaces of glass, mica and platinum", J. Am. Chem. Soc., 40, 1361, (1918).

[14] Sander, B., Fredenslund, A. and Rasmussen, P., "Calculation of vapour-liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation", Chem. Eng. Sci., 41, 1171, (1986).

[15] Nicolaisen, H., Rasmussen, P. and Sørensen, J. M., "Correlation and

prediction of mineral solubilities in the reciprocal salt system $(Na^+, K^+)(Cl^-, SO^{2-}_4)$-$H_2O$ at 0-100°C", J. Chem. Eng. Sci., 48, 3149, (1993).

[16] Thomsen, K., "Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model", J. Pure. Appl. Chem., 77, 531, (2005).

[17] Thomsen, K., Aqueous electrolytes: Model parameters and process simulation, Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark, (1997).

[18] Thomsen, K. and Rasmussen, P., "Modelling of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems", Chem. Eng. Sci., 54, 1787, (1999).

[19] Iliuta, M.C., Thomsen, K. and Rasmussen, P., "Modelling of heavy metal salt solubility using the extended UNIQUAC model", AIChE J., 48, 2664, (2002).

[20] García, A.V., Thomsen, K. and Stenby, E. H., "Prediction of mineral scale formation in geothermal and oilfield operations using the extended UNIQUAC model, Part II. Carbonate-scaling minerals", Geothermics, 35, 239, (2006).

[21] Meissner, H.P. and Tester, J.W., "Activity coefficients of strong electrolytes in aqueous solutions", Ind. Eng. Chem., 11, 128, (1972).

[22] Meissner, H.P. and Kusik, C.L., "Activity coefficients of strong electrolytes in multicomponent aqueous solutions", AIChE J., 18, 294, (1972).

[23] Meissner, H.P., "Prediction of activity coefficients of strong electrolytes in aqueous systems", J. Am. Chem. Soc., Chapter 25, 495, (1980).

[24] Kim, H.T. and Frederick, W.J.,

"Valuation of Pitzer ion interaction parameters of aqueous electrolytes at 25°C, 1. Single salt parameters", J. Chem. Eng. Data, 33, 177, (1988).

[25] Pitzer, K.S. and Kim, J.J., "Thermodynamics of electrolyte,IV. Activity and osmotic coefficients for mixed electrolytes", J. Am. Chem. Soc., 96, 5701, (1974).

[26] Whitfield, M., "The extension of chemical models for sea-water to include trace components at 25 and one atmosphere pressure", Geochimica et Cosmo-chimica Acta, 39, 1545, (1975).

[27] Abramzon, A.A. and Gaukhberg, R.D., "Surface tension of salt solutions", Russ. J. Appl. Chem., 66, 1139, (1993).

[28] Ali, Kh., Ali Shah, A.H., Bilal, S. and Ali Shah, A.H., "Thermodynamic parameters of surface formation of some aqueous salt solutions", J. Colloids Surf., A: Physicochem. Eng. Aspects, 330, 28, (2008).

[29] Matubayasi, N., Matsuo, H., Yamamoto, K., Yamaguchi, S.I. and Matuzawa, A., "Thermodynamic quantities of surface formation of aqueous electrolyte solutions, I. Aqueous solutions of $NaCl$, $MgCl_2$, and $LaCl_3$", J. Colloid Interf. Sci., 209, 398, (1999).

[30] Ali, Kh., Ali Shah, A.H., Bilal, S. and Ali Shah, A.H., "Surface tensions and thermodynamic parameters of surface formation of aqueous salt solutions, III. Aqueous solution of KCl, KBr and KI", Colloids Surf., A: Physicochem. Eng. Aspects, 337, 194, (2009).

[31] Matubayasi, N., Yamamoto, K., Yamaguchi, S.I., Matsuo, H. and Ikeda, N., "Thermodynamic quantities of surface formation of aqueous electrolyte

solutions, III. Aqueous solutions of alkali metal chloride", J. Colloid Interf. Sci., 214, 101, (1999).

[32] Matubayasi, N., Takayama, K. and Ohata, T., "Thermodynamic quantities of surface formation of aqueous electrolyte solutions, IX. Aqueous solutions of ammonium salts", J. Colloid Interf. Sci., 344, 209, (2010).

[33] Matubayasi, N., Tsunetomo, K., Sato, I., Akizuki, R., Morishita, T., Matuzawa, A. and Natsukari, Y., "Thermodynamic quantities of surface formation of aqueous electrolyte solutions, IV. Sodium halides, anion mixtures, and sea water", J. Colloid Interf. Sci., 243, 444, (2001).

[34] Matubayasi, N., Yamaguchi, S.I., Yamamoto, K. and Matsuo, H., "Thermodynamic quantities of surface formation of aqueous electrolyte solutions, II. Mixed aqueous solutions of NaCl and MgCl", J. Colloid and Int. Sci., 209, 403, (1999).