Prediction of Surface Tension in Single and Mixed Electrolyte Solutions

M. Dadras, M.R. Dehghani
Thermodynamics Research Laboratory, School of Chemical Engineering, Iran University of Science & Technology, Narmak, Tehran, Iran

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

* Corresponding author: m_dehghani@iust.ac.ir
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]:

\[-d \sigma_{int} = \Gamma_w d \mu_{w}^{int} + \sum_{i,j} \Gamma_{ij} d \mu_{ij}^{int}\]

(1)

where \( \sigma_{int} \) is equilibrium surface tension, \( \Gamma_w \), \( \Gamma_{ij} \), \( \mu_{w}^{int} \) and \( \mu_{ij}^{int} \) 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:

\[-d \sigma_{int} = \Gamma_w d \mu_{w}^{int} + \Gamma_\infty d \mu_{\infty}^{int}\]

(2)

where, \( \Gamma_w \) and \( \Gamma_\infty \) 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:

\[-d \sigma_{int} = \Gamma_\infty d \ln \mu_{\infty}\]

(3)
In an electrolyte solution, salt chemical potential can be defined as follows:

\[ \mu_{\pm} = \nu_{\pm} \mu_0 + \nu_{\pm} \mu - \]  \hspace{1cm} (4)  

Where, in the molality scale framework we will have:

\[ \mu_{\pm} = \mu_{\pm 0} + RT \ln \left( m_{\pm} \gamma_{\pm} \right) + RT \ln \left( m_{\pm} \gamma_{\pm} \right) \]  \hspace{1cm} (5)  

\[ \mu_{\pm} = \mu_{\pm 0} + RT \ln \left( m_{\pm} \gamma_{\pm}^\nu m_{\pm}^\nu \right) + RT \ln \left( \gamma_{\pm}^\nu \gamma_{\pm}^\nu \right) \]  \hspace{1cm} (6)  

\[ \mu_{\pm} = \mu_{\pm 0} + RT \ln \left( a_{\pm}^\nu a_{\pm}^\nu \right) \]  \hspace{1cm} (7)  

Where, \( \nu = \nu_{\pm} + \nu_{\pm} \), \( a_{\pm} \), \( m_{\pm} \) 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 relation will be obtained:

\[ -d\sigma_{\text{int}} = RT \Gamma_{\pm} d \ln a_{\pm}^\nu \]  \hspace{1cm} (8)  

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

\[ k_{a_{\pm}} \left( 1 - \theta_{\pm} \right) a_{\pm} = k_{d_{\pm}} \theta_{\pm} \]  \hspace{1cm} (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):

\[ \theta_{\pm} = \frac{K_{a_{\pm}} a_{\pm}}{1 + K_{a_{\pm}} a_{\pm}} \]  \hspace{1cm} (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:

\[ \theta_{\pm} = \frac{\int n_{\pm}}{\int n_{\pm}^\text{max}} \]  \hspace{1cm} (11)  

Here \( n_{\pm} \), \( n_{\pm}^\text{max} \) 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 \( A_{\text{int}} \) (the interfacial area) we will have:

\[ \tilde{\theta}_{\pm} = \frac{n_{\pm}}{n_{\pm}^\text{max}/A_{\text{int}}/A} = \frac{\Gamma_{\pm}}{\Gamma_{\pm}^\text{max}} \]  \hspace{1cm} (12)  

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

\[ \tilde{\theta}_{\pm} = \frac{\Gamma_{\pm}^w}{\Gamma_{\pm}^\text{max}} \]  \hspace{1cm} (13)
In which $\Gamma^w_\pm$ and $\Gamma^{w\infty}_\pm$ indicate the interfacial excess and the maximum interface excess respectively when $\Gamma_0 = 0$. Combining Eq. (10) and Eq. (13) leads to the following form:

$$\Gamma^w_\pm = \frac{K_\pm a_s}{1 + K_\pm a_s}$$

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

$$-d\sigma_{hs} = \Gamma^{w\infty}_\pm \frac{K_\pm a_s}{1 + K_\pm a_s} RT d \ln a_s$$

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

$$\sigma_{hs} = \sigma_{hs0} + RT \Gamma^{w\infty}_\pm \ln \frac{1}{1 + K_\pm a_s}$$

In Eq. (16), $\sigma_{hs0}$ is the surface tension of pure water in absence of any electrolyte at the system temperature. $\Gamma^{w\infty}_\pm$ and $K_\pm$ are the model parameters which are determined by minimizing the following objective function:

$$f = \left(\frac{100}{n}\right) \left[ \frac{\gamma_{calc} - \gamma_{exp}}{\gamma_{exp}} \right]$$

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:**

$$\sigma_{hs} = \sigma_{hs0} + \sum RT \Gamma^{w\infty}_\pm \ln \frac{1}{1 + K_\pm a_s}$$

**Model 2:**

$$\sigma_{hs} = \sigma_{hs0} + RT \sum \Gamma^{w\infty}_\pm \ln \left(1 - \frac{K_\pm a_s}{1 + \sum K_\pm a_s}\right)$$

In the above equations, adjustable parameters ($K_\pm$, $\Gamma^{w\infty}_\pm$) 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.

<table>
<thead>
<tr>
<th>Salt</th>
<th>T(K)</th>
<th>$m_{\text{Max}}$</th>
<th>$N$</th>
<th>$\Gamma_{\text{calc}}$</th>
<th>$K$</th>
<th>$\Gamma_{\text{calc}}$</th>
<th>$K$</th>
<th>$\Gamma_{\text{calc}}$</th>
<th>$K$</th>
<th>$\text{AAD} %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO$_2$</td>
<td>291.1</td>
<td>9.84</td>
<td>10</td>
<td>-1.60e-6</td>
<td>1.23</td>
<td>0.18</td>
<td>1.07</td>
<td>0.21</td>
<td>1.51e-6</td>
<td>1.22 0.20</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>303.1</td>
<td>29.09</td>
<td>10</td>
<td>5.89e-7</td>
<td>0.12</td>
<td>0.61</td>
<td>8.04e-7</td>
<td>0.11 0.90</td>
<td>4.91e-7</td>
<td>0.11 0.76</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>298.1</td>
<td>1.80</td>
<td>6</td>
<td>-1.64e-6</td>
<td>3.33</td>
<td>0.15</td>
<td>-1.64e-6</td>
<td>3.53 0.15</td>
<td>-1.60e-6</td>
<td>3.79 0.15</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>298.1</td>
<td>1.90</td>
<td>6</td>
<td>-4.40e-7</td>
<td>5.43</td>
<td>0.18</td>
<td>-4.30e-7</td>
<td>5.57 0.18</td>
<td>-4.53e-7</td>
<td>5.86 0.18</td>
</tr>
<tr>
<td>KOH</td>
<td>293.1</td>
<td>3.80</td>
<td>5</td>
<td>-1.09e-6</td>
<td>0.77</td>
<td>0.30</td>
<td>-1.05e-6</td>
<td>0.74 0.30</td>
<td>-1.00e-6</td>
<td>0.68 0.30</td>
</tr>
<tr>
<td>NH$_4$Cl</td>
<td>292.1</td>
<td>6.77</td>
<td>11</td>
<td>-7.87e-7</td>
<td>2.17</td>
<td>0.10</td>
<td>-8.71e-7</td>
<td>1.55 0.09</td>
<td>-8.56e-7</td>
<td>1.63 0.08</td>
</tr>
<tr>
<td>HCl</td>
<td>293.1</td>
<td>14.98</td>
<td>7</td>
<td>4.84e-7</td>
<td>0.01</td>
<td>0.51</td>
<td>3.43e-7</td>
<td>0.02 0.52</td>
<td>3.02e-7</td>
<td>0.02 0.53</td>
</tr>
<tr>
<td>NaCl</td>
<td>298.5</td>
<td>1.00</td>
<td>9</td>
<td>-3.26e-7</td>
<td>15.26</td>
<td>0.05</td>
<td>-3.09e-7</td>
<td>14.96 0.05</td>
<td>-3.06e-7</td>
<td>16.15 0.05</td>
</tr>
<tr>
<td>KCl</td>
<td>293.1</td>
<td>1.84</td>
<td>6</td>
<td>-8.14e-7</td>
<td>6.37</td>
<td>0.18</td>
<td>-8.41e-7</td>
<td>5.65 0.19</td>
<td>-8.18e-7</td>
<td>6.10 0.19</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>298.5</td>
<td>0.81</td>
<td>10</td>
<td>-2.19e-7</td>
<td>609.77</td>
<td>0.11</td>
<td>-2.03e-7</td>
<td>402.57 0.13</td>
<td>-1.78e-7</td>
<td>559.14 0.13</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>283.1</td>
<td>1.57</td>
<td>4</td>
<td>-2.94e-7</td>
<td>342.50</td>
<td>0.09</td>
<td>-3.48e-7</td>
<td>138.65 0.10</td>
<td>-3.60e-7</td>
<td>192.38 0.10</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>298.1</td>
<td>7.00</td>
<td>9</td>
<td>-5.53e-7</td>
<td>27.90</td>
<td>0.93</td>
<td>-5.12e-7</td>
<td>24.87 0.43</td>
<td>-5.51e-7</td>
<td>13.60 0.77</td>
</tr>
<tr>
<td>SrCl$_2$</td>
<td>293.1</td>
<td>2.82</td>
<td>9</td>
<td>-3.99e-7</td>
<td>756.97</td>
<td>0.18</td>
<td>-4.03e-7</td>
<td>56.35 0.21</td>
<td>-3.99e-7</td>
<td>54.34 0.25</td>
</tr>
<tr>
<td>MnCl$_2$</td>
<td>291.1</td>
<td>3.40</td>
<td>6</td>
<td>-6.50e-7</td>
<td>19.53</td>
<td>0.81</td>
<td>-7.19e-7</td>
<td>12.09 0.71</td>
<td>-7.18e-7</td>
<td>21.74 0.69</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>290.6</td>
<td>1.00</td>
<td>9</td>
<td>-3.60e-7</td>
<td>208.68</td>
<td>0.09</td>
<td>-3.14e-7</td>
<td>14.19 0.09</td>
<td>-4.41e-7</td>
<td>17.12 0.08</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>303.1</td>
<td>0.47</td>
<td>10</td>
<td>-2.13e-7</td>
<td>1035.5</td>
<td>0.05</td>
<td>-1.97e-7</td>
<td>1074.6 0.05</td>
<td>-1.81e-7</td>
<td>1420.5 0.05</td>
</tr>
</tbody>
</table>
| Na$_2$SO$_4$ | 308.1 | 0.90             | 11  | -3.24e-7                | 268.44| 0.08                    | -3.14e-7| 312.11 0.08            | -2.80e-7| 389.28 0.08 |}

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 HNO₃ 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.

<table>
<thead>
<tr>
<th>Salt</th>
<th>T(K)</th>
<th>$m_{\text{max}}$</th>
<th>$N$</th>
<th>Extended UNIQUAC</th>
<th>Pitzer</th>
<th>Meissner</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃</td>
<td>303.15, 298.15, 288.15, 283.15</td>
<td>1.90</td>
<td>6</td>
<td>0.19</td>
<td>0.26</td>
<td>0.19</td>
</tr>
<tr>
<td>KNO₃</td>
<td>303.15, 293.15, 288.15, 283.15</td>
<td>1.80</td>
<td>6</td>
<td>0.24</td>
<td>0.20</td>
<td>0.24</td>
</tr>
<tr>
<td>NaCl</td>
<td>308.15, 303.15, 298.15, 288.15</td>
<td>1.00</td>
<td>9</td>
<td>0.08</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>KCl</td>
<td>303.15, 298.15, 288.15, 283.15</td>
<td>1.84</td>
<td>5</td>
<td>0.60</td>
<td>0.67</td>
<td>0.59</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>308.15, 305.65, 303.15, 300.65, 298.15, 295.65, 290.65, 288.15</td>
<td>1.00</td>
<td>8</td>
<td>0.10</td>
<td>0.12</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>308.15, 298.15, 293.15, 288.15</td>
<td>0.47</td>
<td>10</td>
<td>0.07</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>303.15, 298.15, 293.15, 288.15</td>
<td>0.90</td>
<td>11</td>
<td>0.12</td>
<td>0.17</td>
<td>0.11</td>
</tr>
<tr>
<td>Overall AAD %</td>
<td></td>
<td></td>
<td></td>
<td>0.20</td>
<td>0.23</td>
<td>0.20</td>
</tr>
</tbody>
</table>
Table 3. Prediction of Surface Tension in mixed electrolyte solutions by three models.

<table>
<thead>
<tr>
<th>Salt</th>
<th>T(K)</th>
<th>N</th>
<th>I_max</th>
<th>AAD 1%</th>
<th>AAD 2%</th>
<th>AAD 1%</th>
<th>AAD 2%</th>
<th>AAD 1%</th>
<th>AAD 2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaCl₂·HCl₂</td>
<td>298.15</td>
<td>3</td>
<td>3.49</td>
<td>0.27</td>
<td>0.27</td>
<td>6.10</td>
<td>6.10</td>
<td>0.75</td>
<td>0.75</td>
</tr>
<tr>
<td>SrCl₂·HCl₂</td>
<td>298.15</td>
<td>4</td>
<td>5.86</td>
<td>0.72</td>
<td>0.72</td>
<td>6.49</td>
<td>6.49</td>
<td>0.48</td>
<td>0.48</td>
</tr>
<tr>
<td>CaCl₂·HCl₂</td>
<td>298.15</td>
<td>4</td>
<td>4.54</td>
<td>1.20</td>
<td>1.20</td>
<td>7.75</td>
<td>7.75</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td>KNO₃·HNO₃</td>
<td>303.15</td>
<td>9</td>
<td>28.99</td>
<td>1.59</td>
<td>0.78</td>
<td>8.64</td>
<td>5.63</td>
<td>26.07</td>
<td>12.17</td>
</tr>
<tr>
<td>KNO₃·NH₄NO₃₃</td>
<td>298.15</td>
<td>12</td>
<td>2.79</td>
<td>4.90</td>
<td>5.37</td>
<td>6.89</td>
<td>6.05</td>
<td>4.74</td>
<td>5.30</td>
</tr>
<tr>
<td>KNO₃·NH₄Cl</td>
<td>291.15</td>
<td>10</td>
<td>4.84</td>
<td>1.81</td>
<td>0.49</td>
<td>10.56</td>
<td>1.27</td>
<td>0.58</td>
<td>0.79</td>
</tr>
<tr>
<td>NH₄Cl·(NH₄)₂SO₄</td>
<td>291.15</td>
<td>10</td>
<td>11.18</td>
<td>1.12</td>
<td>3.49</td>
<td>7.68</td>
<td>1.94</td>
<td>2.73</td>
<td>3.80</td>
</tr>
<tr>
<td>(NH₄)₂SO₄·NaNO₃</td>
<td>291.15</td>
<td>9</td>
<td>11.46</td>
<td>1.94</td>
<td>4.22</td>
<td>9.97</td>
<td>3.08</td>
<td>3.53</td>
<td>4.05</td>
</tr>
<tr>
<td>NaCl·Na₂SO₄</td>
<td>298.15</td>
<td>11</td>
<td>0.83</td>
<td>1.03</td>
<td>1.06</td>
<td>0.46</td>
<td>0.45</td>
<td>1.00</td>
<td>1.04</td>
</tr>
<tr>
<td>NaCl·MgCl₂</td>
<td>298.15</td>
<td>9</td>
<td>2.00</td>
<td>0.28</td>
<td>0.68</td>
<td>2.06</td>
<td>0.54</td>
<td>0.33</td>
<td>0.75</td>
</tr>
</tbody>
</table>

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 KNO₃·HNO₃ 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 (NH₄)₂SO₄ - NaNO₃ versus total molality at 291.15. Langmuir &E.UNIQUAC (——), Langmuir & Meissner (-----), Langmuir & Pitzer (— —).
\[ \mu_{ij} \] chemical potentials of electrolyte \( ij \) at interface
\[ \mu_w \] chemical potentials of water at interface
\[ \mu_c \] chemical potentials of electrolyte (cation-anion) at interface
\[ \sigma_{int} \] equilibrium interfacial tension (mN/m)
\[ \sigma_{int}^0 \] equilibrium interfacial tension in absent of electrolyte (mN/m)

References


