A one-parameter equation for predicting densities of aqueous mixed electrolytes

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A new one-parameter equation has been proposed for predicting the densities of aqueous mixed electrolytes. The derivation of the equation is based on the characterization of overall non-ideality in such solutions. The parameter of equation can be correlated well with the ionic interactions and can be supported by corresponding heats of mixing and excess Gibbs free energy of mixing data. The predictions for the densities with the use of the proposed equation are excellent.

A precise knowledge of densities is required in order to obtain the pressure dependence of activity coefficients of electrolytes in aqueous solutions. In dilute aqueous mixed electrolyte solutions, where the long range coulombic forces are predominant, such estimations of densities can be made with confidence using the Young's rule. This method makes use of apparent volumes of pure constituent electrolytes at the ionic strength of the mixture. The apparent volumes, thus obtained can then be converted to give the densities. On the other hand, in concentrated solutions, where the short range forces also play an important role, the calculated values of densities by the Young's rule deviate systematically giving rise to inaccurate predictions. In concentrated solutions, therefore, the appropriate equations derived from the specific interactions theory of Bronsted-Guggenheim and Pitzer are applicable and yield accurate results. The use of both these densities of concentrated electrolyte mixtures is cumbersome, because the theories requires prior knowledge of three or four adjustable parameters.

The purpose of this article therefore is to present a simple and accurate method for estimating the densities of multi-component electrolyte solutions by the use of single adjustable parameter.

Theoretical

Equations: Meissner while predicting activity coefficients in electrolyte solutions, defined a new quantity, i.e. reduced ionic activity coefficient ($\Gamma$) by Eq. (1)

$$\log \Gamma = (\log \gamma^\pm)/(Z_+ Z_-)$$

where $\gamma^\pm$ is mean ionic activity coefficient of a single aqueous electrolyte and $Z$ indicates the ionic charge. Based on this concept, we later on defined the overall reduced ionic activity coefficient ($\Gamma^*$) for mixed electrolyte solutions from the newly derived overall ionic activity coefficient ($\gamma^*$). This relationship is defined by Eq. (2)

$$\log \Gamma^* = \log \gamma^* \left( \frac{\sum \pi_i m_i}{\sum \pi_i} \right) \sum \pi_i Z_i^2$$

where

$$\gamma^* = \sum_{\pi_j} \pi_j \log \gamma^\pm \left/ \sum_{\pi_j} \pi_j m_j \right.$$  \hspace{1cm} (3)

In Eqs (2) and (3), $i$ and $j$ indicate ion and electrolyte, respectively. Value of $J$ for a mixture is always $\leq 2$; $m$ is molality and $v$, the stoichiometry factor of an electrolyte is the sum of ionic stoichiometries and is given by the relation: $v = v_+ + v_-$. It should be noted that $\gamma^*$ characterizes the overall non-ideality of mixed electrolyte solutions. In principle, one can use Gibbs-Duhem equation for establishing a correlation between $\gamma^*$ and the activity of water ($a_w$) in mixed electrolyte solution (see Eq. 4)

$$\log a_w = -\frac{m_w \log \Gamma^*}{2303} - \frac{m_w \log \Gamma^*}{500} + \frac{M_w \log \Gamma^*}{500}$$

where $M_w$ is molecular weight of water, $I$ is the ionic strength and $m_I$ is sum over ionic molalities. Equation (4) can easily be derived with the guidance from the derivations of Meissner. In summary, for convenience, one can write the simple forms of equations for $\Gamma^*$ and $a_w$ as

$$\log \Gamma^* = \sum_{\pi_j} \pi_j \log \Gamma^\pm$$

and

$$\log a_w = \sum_{\pi_j} \pi_j \log a^\pm_{w,j}$$

with $\pi_j$, the ionic strength fraction of $J^{th}$ electrolyte
in mixture being defined as \( y_j = \frac{w_j m_j}{I w_j} \) with valence factor being 1, 3 and 4 for 1-1, 1-2, or 2-1, 2-2 electrolytes respectively, and \( \sum y_j = 1, \Gamma_j^0 \) and \( \Gamma_j^0 \) are the reduced ionic activity coefficient and activity of water of \( J \)th pure constituent electrolyte respectively at the ionic strength of mixture.

Pressure dependence of the above equations for \( \Gamma^*, \gamma^* \) and \( \gamma_\text{H} \) yields the required equations for volumes and subsequently for densities. This is accomplished by writing the volume change on mixing the pure components per 1 kg of water, differentiating Eqs (4) and (6) with respect to pressure and then equating them to give

\[
\Delta V = \frac{1000}{M_w} \frac{RT}{P} \left( \frac{\partial \ln a_i}{\partial P} \right)_{T,N} + \sum m_i R T \left( \frac{\partial \ln a_i}{\partial P} \right)_{T,N} - \frac{1000}{M_w} V_w + \sum m_j V_j
\]

where \( a_j \) is activity of \( J \)th electrolyte in mixture and \( V_w \) is molar volume of water.

Writing an analogous equation as Eq. (7) for mixed electrolytes and using Eqs. (2)-(6), one obtains after simplification

\[
d = \frac{P_j}{(P_i/d_j^0)}
\]

where

\[
P_j = 1000 y_j + m_j M_j
\]

where \( d_j^0 \) is density of pure electrolyte at the ionic strength of mixture. \( M_j \) is molecular weight of \( J \)th electrolyte.

Friedman\textsuperscript{12} using cluster expansion theory derived the Gibbs free energy of mixing for multicomponent electrolyte solutions. Using his conventions and differentiating with respect to pressure one can derive the final expression (10) for computing densities of aqueous mixed electrolytes.

\[
d = \frac{P_j}{(P_i/d_j^0)} + S^{3/2} \prod_{j=2}^{n} y_j
\]

where \( S \) is a parameter specific to the mixture and can be calculated by Eq. (11)

\[
S = \frac{1}{1} \left[ \Delta d \left( \prod_{j=2}^{n} y_j(1-y_j) \right) \right]^{1/2}
\]

with \( \Delta d = d_{\text{exp}} - d \) calculated by Eq. (8). In the case of a symmetric parabola for \( \Delta d \) occurring at \( y = 0.5 \) of a ternary mixture, Eq. (11) reduces to

\[
S = 2\Delta d^{1/2}/I
\]

Results and discussion

In Table 1 are listed the experimental mixture data and the maximum ionic strength to which Eq. (10) was fitted. Table 1 also includes the values of parameter \( S \) along with the standard deviation of fits for the density estimation. In Fig. 1 are plotted the differences [\( \sigma(d) \)] between experimental and calculated densities as a function of \( y \) of an electrolyte for a variety of mixtures consisting of representative charge type electrolytes.

Examination of Table 1 and Fig. 1 demonstrates that the proposed equation predicts the densities of aqueous electrolyte mixtures with remarkable accuracy, having an average standard deviation of 71 ppm obtained from above 300 experimental data points. The standard deviations for the mixtures like NaCl-MgSO\(_4\) and MgCl\(_2\)-Na\(_2\)SO\(_4\) are slightly higher (170 ppm) which are ascribed due to interaction between Mg\(^2+\) and SO\(_4^{2-}\) ions and ion pair formation\textsuperscript{23}. The present equation however could not be examined for quaternary systems for want of experimental data.

<table>
<thead>
<tr>
<th>System</th>
<th>I(_{\text{max}}) (mol kg(^{-1}))</th>
<th>S (ppm)(^{1/2})</th>
<th>(\sigma(d)) (ppm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl-NaBr</td>
<td>4</td>
<td>10.4</td>
<td>22</td>
<td>13</td>
</tr>
<tr>
<td>KCl-KBr</td>
<td>4</td>
<td>10.6</td>
<td>24</td>
<td>14</td>
</tr>
<tr>
<td>NaCl-KCl</td>
<td>4.5</td>
<td>5.9</td>
<td>25</td>
<td>15</td>
</tr>
<tr>
<td>NaBr-KBr</td>
<td>4</td>
<td>5.5</td>
<td>29</td>
<td>14</td>
</tr>
<tr>
<td>KCl-NaBr</td>
<td>4</td>
<td>10.5</td>
<td>35</td>
<td>16</td>
</tr>
<tr>
<td>NaCl-KBr</td>
<td>4.5</td>
<td>24.5</td>
<td>32</td>
<td>17</td>
</tr>
<tr>
<td>KCl-BaCl(_2)</td>
<td>4.5</td>
<td>13.3</td>
<td>85</td>
<td>18</td>
</tr>
<tr>
<td>KCl-CaCl(_2)</td>
<td>4.5</td>
<td>21.5</td>
<td>95</td>
<td>19</td>
</tr>
<tr>
<td>KCl--MgCl(_2)</td>
<td>4.5</td>
<td>18.5</td>
<td>98</td>
<td>20</td>
</tr>
<tr>
<td>KCl--Na(_2)SO(_4)</td>
<td>1.5</td>
<td>21.4</td>
<td>100</td>
<td>21</td>
</tr>
<tr>
<td>NaCl--Na(_2)SO(_4)</td>
<td>3</td>
<td>17.2</td>
<td>53</td>
<td>22</td>
</tr>
<tr>
<td>KCl--KSO(_4)</td>
<td>1.5</td>
<td>17.4</td>
<td>72</td>
<td>21</td>
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<tr>
<td>NaCl--KSO(_4)</td>
<td>1.5</td>
<td>18.8</td>
<td>93</td>
<td>21</td>
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<tr>
<td>NaCl--MgSO(_4)</td>
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<td>19.6</td>
<td>68</td>
<td>22</td>
</tr>
<tr>
<td>MgCl(_2)--Na(_2)SO(_4)</td>
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<td>16.9</td>
<td>53</td>
<td>22</td>
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<tr>
<td>Na(_2)SO(_4)--MgSO(_4)</td>
<td>3</td>
<td>7.6</td>
<td>169</td>
<td>22</td>
</tr>
<tr>
<td>NaCl--MgCl(_2)</td>
<td>3</td>
<td>12.0</td>
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<td>22</td>
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<tr>
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<td>155</td>
<td>22</td>
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<tr>
<td>K(_2)SO(_4)--Na(_2)SO(_4)</td>
<td>1.5</td>
<td>19.2</td>
<td>57</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 1—Summary of experimental data on aqueous mixture densities used for testing Eq. (10)

Average \( \sigma(d) = 71 \) ppm

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But since the reliable experimental data on concentrated brines composed of aqueous NaCl-KCl-CaCl₂-MgCl₂ have recently become available, it is desirable to test the proposed relationship in this case. These data cover the ionic strength range between 8.3 and 9.6 mol kg⁻¹, where the individual univalent electrolytes like NaCl and KCl do not exist due to solubility limits. If the densities of both these electrolytes are extrapolated to desired ionic strength with the help of a simple polynomial expressed elsewhere, one finds that the proposed relationship predicts the densities on an average to about 466 ppm, which is an excellent achievement in such high concentration region.

It is interesting to note that the values of S both for aqueous NaCl-NaBr and KCl-KBr are approximately same. Similarly, the values of S are identical in the cases of aqueous NaCl-KCl and NaBr-KBr systems. This indicates that the mixing of Cl⁻ and Br⁻ ions in the presence of Na⁺ and K⁺ ions is the same. The same situation prevails for the mixing of Na⁺ and K⁺ ions in the presence of common anions like Cl⁻ and Br⁻ ions. These observations along with those made in other univalent electrolyte mixtures are supported by the heats of mixing data of Wood and Smith and Young et al. The strength of interactions in terms of the magnitude of S values between Cl⁻ and Br⁻ ions can easily be compared with that of Na⁺ and K⁺ ions on the basis of heats of mixing data of Wood and Smith. Such observations also hold true in the case of either Na⁺ or K⁺ ion mixing in the presence of Cl⁻ or SO₄²⁻ ions. For the mixing of reciprocal electrolytes like NaCl-KBr and KCl-NaBr, etc., it is of interest to note that the sign of S values changes. This is again supported by the heats of mixing and free energy of mixing data. The excess volume interaction parameters evaluated by Millero et al. for Cl⁻-SO₄²⁻ and Na⁺-Mg²⁺ also support the observations recorded in Table 1.

The equations can easily be applied to other properties like compressibilities and expansibilities after appropriate differentiations.

References
16 Kumar A, J Chem Engng Data, (Accepted).