Heats of Dilution of Some Uni-univalent Electrolytes in Water & the Transition Model

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Relative partial molar enthalpies, \( \Delta L \), and apparent molar enthalpies, \( \Phi_L \), of some 1:1 electrolytes in water have been calculated at 298.15 K on the basis of a model that assumes that each electrolyte ion has a definite probability to be in either the Debye configuration or in the lattice configuration. The calculated \( \Delta L \) and \( \Phi_L \) values compare very well with the corresponding experimental values. The heats of dilution of NaCl, HCl, NaBr and KCl calculated from their \( \Phi_L \) values also agree well with their corresponding experimental values.

The properties of strong electrolytes in dilute aqueous solutions have been interpreted in terms of Debye-Hückel theory. A close examination of the statistical mechanical foundations of this theory has led to an appreciation of its limitations and this in turn has led to the development of more sophisticated theories of electrolytic behaviour. Nevertheless the latter theories have made only limited headway towards describing thermochemical properties of electrolytes in solution in the concentration range of practical interest. Bär15 has recently made an effort in this direction but he assumes that ions in an electrolyte have loose lattice configuration and that this holds even for very dilute solutions. While recent neutron diffraction studies on very concentrated electrolyte solutions suggest that ions in these solutions tend to acquire a loose lattice structure, it is highly unrealistic to expect that the ions would continue to be in the loose lattice structure even in dilute solutions. The loose lattice structure in concentrated electrolyte solutions may be taken to suggest that the ions in these lattice have a tendency to leave a particular lattice configuration and enter another one and so may pass through a situation very similar to the Debye configuration. A similar situation may be visualized for very dilute solutions; the time average configuration points towards some sort of lattice arrangement in very dilute solutions. This would then mean that each electrolyte ion will have a certain definite probability to be in either the Debye configuration or the lattice configuration so that the difference between a concentrated and a dilute electrolyte solution is merely of degree rather than of kind. Based on statistical mechanical considerations it has been shown that the probability that an ion is in a Debye configuration is given by \( e^{-1.5m} \) where \( m \) is the molality of the solution so that the mean molal ionic activity coefficient of an electrolyte is expressed by Eq (1)

\[
\log (\gamma_i) = e^{-1.5m} \left( \log \gamma_i \right)_{\text{Debye}} + (1 - e^{-1.5m}) \left( \log \gamma_i \right)_{\text{lattice}} - \log \left( 1 + \frac{vmM_i}{1000} \right)
\]  

where all the terms have their usual significance. Equation (1) has been shown to describe very well not only the activity coefficients of a number of 1:1 and 2:1 electrolytes in water but also the partial molar volumes of a number of 1:1 electrolytes in water at 298.15 K. The basic arguments of this model (called the transition model) have also been utilized to predict very well the mean molal activity coefficient of an electrolyte A or B in a ternary (A + B + H\(_2\)O) solution. This paper is concerned with evaluating relative partial molar enthalpies, \( \Delta L \), apparent molar enthalpies and hence the heats of dilution of some 1:1 electrolytes in water at 298.15 K, using transition model in water at 298.15 K. 

Results and Discussion

The partial molar Gibbs free energy for an electrolyte in solution is given by

\[
\bar{G}_2 = \bar{G}_2 + RT \ln f^*_x X^*_x \quad \ldots (2)
\]

where \( f^*_x \) is the mean mole fraction ionic activity coefficient and \( X^*_x \) is its corresponding mole fraction. Since \( \frac{\partial}{\partial T}(\Delta G/T) = -\Delta H/T^2 \), Eq. (2) yields

\[
-vRT^2 \frac{\partial}{\partial T}(\ln f_x) = \bar{H}_2 - H^* = \Delta L \quad \ldots (3)
\]

where \( \Delta L \) is the relative partial molar enthalpy of the electrolyte

Further as

\[
\ln (\gamma_x) = \ln f_x - \ln (1 + \frac{vmM_i}{1000}) \quad \ldots (4)
\]

Eq. (1) reduces to

\[
\ln f_x = e^{-1.5m} \ln (f_x)_{\text{Debye}} + (1 - e^{-1.5m}) \ln (f_x)_{\text{lattice}} \quad \ldots (5)
\]
SINGH: HEATS OF DILUTION & TRANSITION MODEL

so that

\[
L_2 = e^{-1.5m}(L_2)_{\text{Debye}} + (1 - e^{-1.5m})(L_2)_{\text{lattice}}
\]

But \( \ln(f_L)_{\text{lattice}} \) is expressed \(^\text{15} \) by

\[
\ln(f_L)_{\text{lattice}} = -2.3026 AC^{1/3} + 2.3026 BC
\]

where \( A \) is a constant characteristic of the particular lattice assumed for the electrolyte in solution and for a face centred cubic lattice (as is the case here for 1:1 electrolytes) at 298.15 K it has a value \(^\text{15} \) of 0.28894 while the parameter \( B \) is characteristic of the electrolyte and can be readily evaluated \(^\text{15} \) from an analysis of its mean molality activity coefficient data in the concentration range 0.1 \( m \) to 1.5 \( m \) so that

\[
(L_2)_{\text{lattice}} = RT^2(2.3026) \left[ \frac{\partial A}{\partial T} C^{1/3} \right. \\
\left. + \left( \frac{A}{3C^{7/3} - B} \right) \left( \frac{\partial C}{\partial T} - C \frac{\partial B}{\partial T} \right) \right]
\]

Further \( \frac{\partial A}{\partial T} \) at 298.15K has a value \(^\text{19} \) 3.56547 \( \times 10^{-4} \) so that \( L_2 \) for 1:1 electrolyte at this temperature is given by Eq. (9).

\[
L_2 = e^{-1.5m} \left[ 708 \sqrt{\frac{3}{2}} \sum Z_i^2 C \right] \\
\left( 1 + ab \sqrt{\frac{3}{2}} \sum Z_i^2 \right)
\]

\[
+ (1 - e^{-1.5m}) (812826.85) \left( 3.56547 \times 10^{-4} C^{1/3} \right)
\]

\[
+ (0.096313 C^{-2/3} - B) \left( \frac{\partial C}{\partial T} - \frac{\partial B}{\partial T} \right) C
\]

The quantity \( ab \) is Debye original expression for \( L_2 \); it has values \(^\text{14} \) between 1.3 and 1.5 and for the present analysis we have taken \( ab = 1.4 \). We now consider some characteristics of Eq. (9).

For very dilute solutions \( (C < 0.005 \text{ molar}) \), the lattice contributions to \( L_2 \) would be negligible so that \( L_2 \) would be linear in \( \sqrt{C} \), as has indeed been observed \(^\text{14} \). For comparatively more concentrated solutions \( (C > 0.3 \text{ molar}) \), the lattice contributions to \( L_2 \) out weigh those due to Debye so that \( L_2 \) should be linear in \( C^{1/3} \). Equation (9) thus corrects the lattice theory \(^\text{15} \) to allow for infinite dilution effects.

We now consider the effectiveness of Eq. (9) to predict \( L_2 \) for some 1:1 electrolytes for which the relevant data in water are available at 298.15 K. This requires values of \( \frac{\partial C}{\partial T} \) and \( \frac{\partial B}{\partial T} \) for the electrolyte. \( \frac{\partial C}{\partial T} \) values for an electrolyte at 298.15 K can be calculated from the relation (10)

\[
(\frac{\partial C}{\partial T})_{T=298} = (C_{30} - C_{20})/(30 - 20)
\]

where \( C_{30} \) and \( C_{20} \) refer to the concentration of the electrolyte in water at 30 and 20°C respectively and which could be computed from the parameters given by Harnd and Owen \(^\text{16} \) to convert molality to molarity at various temperatures. Alternatively \( \frac{\partial C}{\partial T} \) values for an electrolyte can also be calculated from the expression (11)

\[
\frac{\partial C}{\partial T} = m \left( \frac{\partial}{\partial t} d_0 \right) - m^2 \left( \frac{\partial}{\partial t} A^1 \right)
\]

while the parameter \( B \) is characteristic of the electrolyte at this temperature. \( \frac{\partial C}{\partial T} \) values as a function of \( C \) or \( m \) at 298-15K for a 1:1 electrolyte from Eq. (9) then requires a knowledge of \( \frac{\partial B}{\partial T} \) for the electrolyte. In principle \( \frac{\partial B}{\partial T} \) value, which is characteristic of an electrolyte, can be evaluated if \( L_2 \) value for the electrolyte at one concentration alone is known but as it makes significant contribution to \( (L_2)_{\text{lattice}} \) it should preferably be evaluated by utilizing any \( L_2 \) value of the electrolyte in the concentration range in which the lattice model holds. For this purpose we expressed Eq. (8) as

\[
3.5655 \times 10^{-4} C^{1/3} + (9.6313 \times 10^{-2} C^{-2/3} - B)
\]

and observed that the left hand side of Eq. (12) was effectively linear in \( C \) with a slope \( \frac{\partial B}{\partial T} \) in the concentration range 0.5 \( \leq C \leq 2.0 \) (corresponding to 0.5 \( \leq m \leq 1.8 \)) only for most of the 1:1 electrolytes for which \( L_2 \) values \(^\text{19} \) in the range 0.5 \( \leq m \leq 3.5 \) were available at 298.15K. A safer anchoring \( L_2 \) value to evaluate \( \frac{\partial B}{\partial T} \) for a 1:1 electrolyte at 298.15K from Eq. (9) would then be \( L_2 \) value in the range 0.8 \( \leq m \leq 1.8 \) for the electrolyte. For the the present analysis we evaluated \( \frac{\partial B}{\partial T} \) value for a 1:1 electrolyte by fitting \( L_2 \) value at 298.15K for its one molar solution in water to Eq. (9). This value of \( \frac{\partial B}{\partial T} \) was next used to evaluate \( L_2 \) from Eq. (9) for different concentrations of the electrolyte. \( L_2 \) values so obtained for various electrolytes are recorded in Table 1 and are also compared with their corresponding literature \(^\text{19} \) values.

Examination of Table 1 shows that considering the uncertainties in evaluating \( L_2 \) from the experimental results, the agreement between the calculated and the literature \( L_2 \) values is reasonably good. However, in the transition range \( (L_2)_{\text{theoretical}} \) \( \leq (L_2)_{\text{Experimental}} \) for most of these 1:1 electrolytes. Since \( (L_2)_{\text{Debye}} > (L_2)_{\text{lattice}} \) in this range, the divergence between the theoretical and the experimental \( L_2 \) values may be traced to the model
slightly underestimating the probability \( \pi \) that an ion is in Debye configuration compared to the probability that the ion is in lattice configuration.

We now use our \( \bar{L}_2 \) values to evaluate relative apparent molar enthalpy, \( \phi_L \), of a 1:1 electrolyte. For a two component system, containing \( n_1 \) mol of solvent and \( n_2 \) mol of the electrolyte, we have

\[
L = n_2 \bar{L}_1 + n_2 \bar{L}_2 = n_2 \phi_L 
\]

Differentiation of Eq. (13) with respect to \( n_2 \) at constant temperature and \( n_1 \) yields

\[
\frac{\partial L}{\partial n_2} = \frac{\partial \bar{L}_2}{\partial n_2} = n_2 \frac{\partial \phi_L}{\partial n_2} = \frac{\partial}{\partial m}(m \phi_L) \tag{14}
\]

where \( m \) is the molality of the solution.

We now express \( \bar{L}_2 \) as

\[
\bar{L}_2 = \alpha m^{1/2} + \beta m + \gamma m^{3/2} \tag{15}
\]

so that

\[
\frac{\partial}{\partial m}(m \phi_L) = \alpha m^{1/2} + \beta m + \gamma m^{3/2} \tag{16}
\]

Integration of Eq. (6) yields

\[
\phi_L = \frac{1}{m} \int_0^m (\alpha m^{1/2} + \beta m + \gamma m^{3/2}) \, dm 
\]

\[
= \frac{2}{3} \alpha m^{1/2} + \frac{\beta}{2} m^2 + \frac{\gamma}{5} m^{3/2} \tag{17}
\]

The \( \phi_L \) values for the various electrolytes calculated according to Eq. (17) are recorded in Table 1 and they compare well with their corresponding literature values. The parameters \( \alpha \), \( \beta \) and \( \gamma \) of Eq. (17) were evaluated by a least square fit of our \( \bar{L}_2 \) values to Eq. (15). As a further check on our \( \phi_L \) values, we evaluated heats of dilution \( \Delta H_D \) using the relation

\[
\Delta H_D = \phi_L(m_f) - \phi_L(m_i) \tag{18}
\]

where \( \phi_L(m_f) \) and \( \phi_L(m_i) \) refer to \( \phi_L \) values at the final and the initial molality of the solution.

Fortier et al.\(^{21}\) have made very precise \( \Delta H_D \) measurements on aqueous solutions of sodium.
Table 2—Comparison of Heats of Dilution ($\Delta H_D$) at 298.15K of Some 1:1 Electrolytes in Water, Calculated According to Eq. (15), with the Corresponding Literature Values

<table>
<thead>
<tr>
<th>$m_i$</th>
<th>$m_f$</th>
<th>$\Delta H_D$ (Cal. mol$^{-1}$)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>calc.</td>
<td>Parker$^{19}$</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.01075</td>
<td>0.00525</td>
<td>-11.36</td>
<td>-10.71</td>
</tr>
<tr>
<td>0.0197</td>
<td>0.00979</td>
<td>-13.85</td>
<td>-12.81</td>
</tr>
<tr>
<td>0.06209</td>
<td>0.03068</td>
<td>-15.55</td>
<td>-14.24</td>
</tr>
<tr>
<td>0.09999</td>
<td>0.04933</td>
<td>-13.20</td>
<td>-12.79</td>
</tr>
<tr>
<td>0.1601</td>
<td>0.07902</td>
<td>-7.18</td>
<td>-8.32</td>
</tr>
<tr>
<td>0.3621</td>
<td>0.1813</td>
<td>17.47</td>
<td>12.76</td>
</tr>
<tr>
<td>0.5000</td>
<td>0.2464</td>
<td>34.03</td>
<td>27.75</td>
</tr>
<tr>
<td>0.6000</td>
<td>0.3000</td>
<td>44.62</td>
<td>38.72</td>
</tr>
<tr>
<td>0.7199</td>
<td>0.3647</td>
<td>69.25</td>
<td>51.67</td>
</tr>
<tr>
<td>0.9999</td>
<td>0.5023</td>
<td>80.78</td>
<td>80.19</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2778</td>
<td>0.1389</td>
<td>-54.00</td>
<td>-56.00</td>
</tr>
<tr>
<td>0.5556</td>
<td>0.2778</td>
<td>-78.67</td>
<td>-83.00</td>
</tr>
<tr>
<td>0.1389</td>
<td>0.2778</td>
<td>-132.66</td>
<td>-139.00</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2778</td>
<td>0.1389</td>
<td>7.50</td>
<td>3.0</td>
</tr>
<tr>
<td>0.5556</td>
<td>0.2778</td>
<td>40.24</td>
<td>35.0</td>
</tr>
<tr>
<td>0.5556</td>
<td>0.1389</td>
<td>47.74</td>
<td>34.0</td>
</tr>
<tr>
<td>Sodium bromide</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.0502</td>
<td>0.0013</td>
<td>-58.85</td>
<td>-60.0</td>
</tr>
<tr>
<td>0.0502</td>
<td>0.0026</td>
<td>-52.26</td>
<td>-54.0</td>
</tr>
<tr>
<td>0.0026</td>
<td>0.0026</td>
<td>-63.61</td>
<td>-61.0</td>
</tr>
<tr>
<td>0.00052</td>
<td>-54.94</td>
<td>-48.0</td>
<td></td>
</tr>
</tbody>
</table>

chloride. The $\Delta H_D$ values (Table 2) as evaluated from our $\varphi_L$ data at 298.15K compare very well with their data$^{21}$. On the other hand while $\Delta H_D$ values for aqueous hydrochloric acid as calculated from our $\varphi_L$ data agree well with those due to Richard and Rowe$^{22}$, the same, however, is not true of $\Delta H_D$ values for potassium chloride in water$^{22}$. For potassium chloride in water $\Delta H_D$ values compare reasonably well with those calculated from $\varphi_L$ values reported by Parker$^{20}$. Our $\varphi_L$ values for sodium bromide in water yield $\Delta H_D$ values that do not compare well with those due to Hammerschmid and Robinson$^{23}$ but they agree well with those calculated from the $\varphi_L$ values reported by Parker$^{20}$.

Thus from a single $L_2$ value for an electrolyte at $m = 1.0$ (which could be easily achieved from the temperature variation of e.m.f of suitable cells) it is possible to predict $L_2$, $\varphi_L$ and hence $\Delta H_D$ for the electrolyte over a considerable range of concentrations.

References

1 (a) Harned H S & Owen B B, *The physical Chemistry of electrolyte solutions* (Reinhold, New York) 1958; (b) pp 77; (c) 525; (d) 501; (e) 705; (f) 709-710; (g) 707-708, 727.