Estimation of Apparent Molal Compressibilities of Ions, Salts & Mixtures in Pure Water & Sea Water Using Brønsted-Guggenheim Theory

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The Brønsted-Guggenheim theory has been used for estimating apparent molal compressibilities of ions, salts and mixtures and sound velocities in pure water and sea water at 25°C. The cation-anion interactions are considered predominant and cation-cation and anion-anion interactions are completely neglected. The interaction coefficients obtained from single salt analysis are used in calculations for mixtures of salts in pure water and sea water.

We have recently shown1 that Brønsted-Guggenheim (B-G) theory can accurately predict the apparent molal volumes and densities of ions, salts and mixtures in pure water and sea water at 25°C. In the present paper, this theory has been extended to estimate the other volume properties, viz. apparent molal compressibilities ($\phi_k$) of ions, salts and mixtures and relative sound velocities $(U-U_o)$ in the multicomponent mixtures of NaCl–CaCl₂ in pure water and sea water. The parameters obtained from single salts are employed for mixtures in pure and sea water media. For this purpose, the moderate ionic strengths of 0.3, 0.5 and 1.0 mol kg$^{-1}$ are chosen and higher concentrations completely avoided.

Proposed Version of B-G Theory and Method of Calculations
The equation of apparent molal volume$^1$ can be differentiated with respect to pressure to obtain the expression for the apparent molal compressibility ($\phi_k$) of a salt $M^r_\text{M}X^r_\text{X}$ as

\[
\phi_k = \phi_k^0 + \frac{A_k \sum Z_i^2 I_i^{1.2}}{3(1 + I^{1.2})} + \frac{1}{2} \sum_{M} B_{MX} \frac{m_M}{m_X} \quad \ldots \ldots (1)
\]

where $\phi_k$ and $\phi_k^0$ are apparent molal compressibilities (cm$^3$ mol$^{-1}$ bar$^{-1}$) at a given molality and at infinite dilution. $A_k$ is Debye–Huckel limiting slope (2.41 × 10$^{-4}$ cm$^3$ kg$^{-1}$ mol$^{-1}$ 2 bar$^{-1}$) and $I$ refers to the ionic strength (in mol kg$^{-1}$).

$B_{MX}$ is the B-G interaction coefficient, accounting for cation-anion interactions and is given by Eq.(2).

\[
B_{MX} = B^K(0) + B^K(1)I + B^K(2)I^2 \quad \ldots \ldots (2)
\]

$r_M$ and $r_X$ are mol of $M$ and $X$ per mol of salt respectively.

\[
v = v_M + v_X \quad \ldots \ldots (3)
\]

Ionic apparent molal compressibility can be expressed by Eq.(4)

\[
\phi_k = \phi_k^0 + \frac{Z_i^2 A_k I_i^{1.2}}{3(1 + I^{1.2})} + \frac{1}{2} \sum_{j} B_{ij} m_j \quad \ldots \ldots (4)
\]

where $B_{ij}^K$ is B-G parameter or coefficient for cation-anion pair, $m_j$ is molality and $Z_i$ is the charge on ion. The summation is over all the ions with charge opposite to that on ion $i$.

Single salt analysis
$\phi_k$ data of a salt are fed into computer along with their respective molality. Equation (1) is then used to give interaction parameter $B_{MX}^K$ in terms of $B^K(0), B^K(1)$ and $B^K(2)$ using a least square programme. These parameters can now be used in calculations for mixtures in pure water and sea water.

Calculations in pure water
The $B_{MX}^K$ coefficients for each pair are used in Eq.(4) to give ionic apparent molal compressibility. One can use Young rule$^4$ to give $\phi_{Kj}$, the apparent molal compressibility of a salt in the mixture as in Eq.(5)

\[
\phi_{Kj} = \sum_i v_i \phi_{ki} \quad \ldots \ldots \ldots \ldots \ldots (5)
\]

$\phi_{Kj}$ gives the mean apparent molal compressibility ($\phi_k^*$) as

\[
\phi_k^* = \frac{\sum_j m_j \phi_{kj}}{\sum_j m_j} \quad \ldots \ldots \ldots \ldots (6)
\]
Table 1—Bronsted-Guggenheim Coefficients Calculated using Eq. (1)

<table>
<thead>
<tr>
<th>Salt</th>
<th>( -\varphi ) K ( \text{cm}^3 \text{mol}^{-1} \text{bar}^{-1} )</th>
<th>( -\varphi(0) ) ( \times 10^4 )</th>
<th>( \beta^b(1) ) ( 10^5 )</th>
<th>( \beta^b(2) ) ( 10^6 )</th>
<th>( \sigma \times 10^4 ) ( \text{cm}^3 \text{mol}^{-1} \text{bar}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>( 48.30 \pm 0.20 )</td>
<td>( 8.33 \pm 0.39 )</td>
<td>(-12.96 \pm 0.18 )</td>
<td>( 10.26 \pm 2.34 )</td>
<td>( 0.21 )</td>
</tr>
<tr>
<td>CaCl_2</td>
<td>( 91.25 \pm 0.71 )</td>
<td>( 9.70 \pm 0.55 )</td>
<td>(-4.50 \pm 0.64 )</td>
<td>( 0.89 \pm 0.20 )</td>
<td>( 0.81 )</td>
</tr>
</tbody>
</table>

Table 2—R MS D(\( \sigma \)) for Relative Sound Velocities \( (U-U_0) \) and Mean Apparent Molal Compressibilities \( (\varphi_K) \) in Pure Water and Sea Water

<table>
<thead>
<tr>
<th>Ionic Strength†</th>
<th>( U-U_0 ) ( (\text{cm} \text{s}^{-1}) )</th>
<th>( \varphi_K \times 10^4 ) ( (\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}) )</th>
<th>( \varphi_K \times 10^4 ) ( (\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>Sea water</td>
<td>Pure water</td>
<td>Sea water</td>
</tr>
<tr>
<td>0.3</td>
<td>28</td>
<td>32</td>
<td>0.80</td>
</tr>
<tr>
<td>0.5</td>
<td>50</td>
<td>55</td>
<td>0.95</td>
</tr>
<tr>
<td>1.0</td>
<td>80</td>
<td>89</td>
<td>0.99</td>
</tr>
</tbody>
</table>

†Values in pure water

Table 3—Apparent Molal Compressibilities of NaCl and CaCl\_2 \( (\varphi_K) \) in Pure Water and Sea Water at 25 C

<table>
<thead>
<tr>
<th>( \gamma_b )</th>
<th>Pure water</th>
<th>Sea water</th>
<th>Pure water</th>
<th>Sea water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic strength† = 0.3</td>
<td>( 48.06 )</td>
<td>( 43.19 )</td>
<td>( 89.19 )</td>
<td>( 80.56 )</td>
</tr>
<tr>
<td>Ionic strength† = 0.5</td>
<td>( 48.24 )</td>
<td>( 43.49 )</td>
<td>( 89.51 )</td>
<td>( 81.11 )</td>
</tr>
<tr>
<td>Ionic strength† = 1.0</td>
<td>( 48.42 )</td>
<td>( 43.79 )</td>
<td>( 89.82 )</td>
<td>( 81.67 )</td>
</tr>
</tbody>
</table>

†Values in pure water (mol kg\(^{-1}\))

Table 4—\( \varphi^b \) and \( U-U_0 \) in Pure Water and Sea Water

<table>
<thead>
<tr>
<th>Ionic strength† = 0.3</th>
<th>( \varphi^b \times 10^4 )</th>
<th>( U-U_0 ) ( (\text{cm}^3 \text{mol}^{-1} \text{bar}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>Sea water</td>
<td>Pure water</td>
</tr>
<tr>
<td>54.35</td>
<td>20.12</td>
<td>1586</td>
</tr>
<tr>
<td>60.23</td>
<td>20.47</td>
<td>1398</td>
</tr>
<tr>
<td>69.17</td>
<td>20.77</td>
<td>1212</td>
</tr>
</tbody>
</table>

Calculation in sea water

The procedure is exactly the same as in the case of apparent molal volume. Sea water recipe of Millero\(^5\) was used and final concentrations of the systems after adding aq. NaCl – CaCl\(_2\) of ionic strengths of 0.3, 0.5 and 1.0 mol kg\(^{-1}\) were calculated. The calculations were performed for each experimental point of Kumar et al.\(^6\) but for the sake of illustration only three experimental points (\( \gamma_b = 0.35, 0.55 \) and 0.75, where \( \gamma_b \) is the ionic strength ratio of CaCl\(_2\)) were chosen.

The B-G coefficients for Na\(^+\), Ca\(^{2+}\) and Cl\(^-\) obtained from single salt analysis were used along with those of \( \text{SO}_4^{2-}, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{B(OH)}_4^-, \text{Br}^- \) and F\(^-\), Mg\(^{2+}\), Sr\(^{2+}\) and K\(^+\) reported by Millero\(^5\). The contribution of HCO\(_3^-, \text{CO}_3^{2-}, \text{B(OH)}_4^-\), Br\(^-\) and F\(^-\) towards total apparent molal compressibility was found very small and hence neglected.

One can now use Eq. (4) to give \( \varphi_K \) of Na\(^+\), Ca\(^{2+}\) and Cl\(^-\) in a mixture. \( \varphi_K \) values thus obtained can be converted to give \( \varphi_K \) for NaCl and CaCl\(_2\) using Eq. (5). The mean apparent molal compressibility, \( \varphi^b_\text{MS} \) is calculated by Eq. (8).

\[
\varphi^b_\text{MS} = \frac{\sum m_i \varphi_{K_i}}{\sum m_i} \quad \ldots (8)
\]
Sound velocity in sea water \((U_s)\) is then expressed by Eq. (9)

\[
U_s = \frac{1000}{d} \left[ 1000 + \sum \frac{m_i M_i}{U_0 d_0^2 + \sum m_i \phi_{K_i}} \right]^{1/2} \quad \ldots (9)
\]

where \(\sum\) is over ions and \(M_i\) is molecular weight of ion.

**Results and Discussion**

Table 1 lists the B-G coefficients for NaCl and CaCl\(_2\) along with the standard deviation \(\sigma\). Data for NaCl and CaCl\(_2\) were taken from elsewhere\(^6,7\). \(\phi_K\) data for NaCl fit better than those for CaCl\(_2\). The poor fit in the case of CaCl\(_2\) is due to the change in hydration sphere of Ca\(^{2+}\) ions in the concentration range above 1 molal\(^8\). This has been confirmed by neutron scattering studies of Hewish et al.\(^9\), and activity coefficient studies\(^10\). The mathematical function for such a change is not easy to be accommodated in B-G theory. All the coefficients inspite of the error involved for both the salts are retained for performing the pairwise calculations.

The performance of this theory in pure water is summarised in Table 2, where calculated values of the density and mean apparent molal volumes are compared with experimental data\(^6\), in terms of root mean square deviation \(\sigma\) for \(U - U_0\) and \(\phi_K\) to within 2 and 1\(^\circ\), respectively. The predictions in terms of the theory can be further improved, if the cation-cation interactions are taken into account. However, it has been neglected for the sake of simple and straightforward calculations of interaction coefficients in sea water media.

The results of calculations in sea water are shown in Table 2. It is clear from \(\sigma\) values that the predicted \(U - U_0\) and \(\phi_K\) values are fairly in good agreement with experimentally observed values\(^11\). Table 3 lists \(\phi_K\) of NaCl and CaCl\(_2\) in pure water and sea water while Table 4 shows the \(U - U_0\) and \(\phi_K\) in pure water and sea water at the concentrations studied. The trend in the values of the ionic properties can be explained on the basis as has been done in the case of apparent molal volume\(^1\).

In conclusion, it has been demonstrated that B-G theory predicts the apparent molal compressibility fairly accurately and it is hoped that this theory will equally apply in estimating the expansibility of such mixtures.

**Acknowledgement**

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**References**