A Cryoscopic Study of Ionic Association in Bivalent Metal Sulphates using Saturated Aqueous Solutions

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The classical dissociation constants of a number of bivalent metal sulphates have been determined at three ionic strengths by the method previously used by the author. The dependence of pK values on ionic strength has been expressed with the aid of the Debye-Hückel formula and the thermodynamic dissociation constants have been extrapolated.

A considerable amount of work has been done in the field of incomplete dissociation of higher charge type electrolytes in water. Spectrophotometric methods have frequently been used but in most cases the evaluation of the degree of association has been based on deviations from the Debye-Hückel theory or other theories based on similar models. This type of procedure always includes some arbitrary assumptions, e.g. about the activities or conductivities of the ions or associated molecules. These theories give reliable approximations for the changes in the activity or conductivity of ions only in very dilute solutions in which the degree of association often is very slight. Very accurate measurements are needed but still leave some doubt about the interpretation of the results. However, most investigations support the existence of association in higher charge type electrolytes and give association constants of the same order of magnitude. Nevertheless, this ionic association has not been generally accepted and papers have frequently been published, in which complete dissociation has been assumed in conditions where it is certainly not valid. Further work is required in this field to draw attention to these phenomena and to provide additional information. In particular, there is a need for the development of methods that do not involve arbitrary assumptions about ion activities and allied properties.

METHOD

The approach employed in this paper is based on the behaviour of a mixture of ice and water saturated with an electrolyte like a one component solvent in cryoscopic measurements. The author has previously introduced the use of such "solvent" in the study of the incomplete dissociation of

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some bivalent metal sulphates at one ionic strength. This paper describes the extension of this study to three ionic strengths. These "solvents" themselves contain a certain concentration of ions, dependent on the saturating electrolyte, and the activity factors of the ions in them will therefore change only slightly or will remain almost constant when considerable amounts of some other electrolyte are added, provided that the saturating electrolyte is soluble to raise the ionic strength, about up to 0.05 or more. The depression of the freezing point of this kind of "solvent"-ice mixture is therefore almost directly proportional to the sum of the concentrations of ions, and associated ions, other than those arising from the saturating electrolyte. Hence the method provides a means of estimating the sum of the concentrations of these. When these and the corresponding stoichiometric concentrations of an electrolyte are known, it is possible to find the dissociation constant for this electrolyte by extrapolation. Data obtained from solutions containing relatively high concentrations of the electrolyte being studied and showing a relatively large effect due to the ionic association can be used for the extrapolation. This method has been applied here to the study of 2—2 type electrolytes but, it can be used to study the association of any type of electrolyte.

For a water-ice mixture saturated with an electrolyte, the dependence of the freezing point depression $\Delta T$, on $\Sigma m_i$, the sum of the concentrations of the ions and molecules that are not common with those arising from the saturating electrolyte is given by

$$\Sigma (dm_i + m_i d\eta_i) = d(\Delta T)/K^c_t$$

When the changes in activity coefficients are small the expression

$$\Sigma m_i \approx \Sigma \overline{m}_i \equiv \Delta T/K^c_t$$

(2)

gives a good approximation, $\Sigma \overline{m}_i$, for $\Sigma m_i$. However, from eqn. (1) it is essential, that

$$\lim_{m_s \to 0} \Sigma m_i = \Sigma m_i$$

(3)

where $m_s$ is the stoichiometric concentration of added electrolyte.

The molar depression of the freezing point of a saturated solution, $K^c_t$, is best derived from the freezing point depressions of 1—1 electrolytes for which the association is negligible. Extrapolation of the values given by

$$K_t \equiv \Delta T/2m_s$$

(4)

to infinite dilution for the added 1—1 electrolyte gives the value of $K^c_t$.

In solutions of a bivalent metal sulphate $\text{MSO}_4$, there may be $\text{MSO}_4$ molecules and $\text{M(SO}_4)_2^{2-}$ ions present due to ion-pair formation in addition to $\text{M}^{2+}$ and $\text{SO}_4^{2-}$ ions. If the dissociation constants are

$$k_1 = [\text{M}^{2+}][\text{SO}_4^{2-}] / [\text{MSO}_4]$$

(5)

and

$$k_2 = [\text{MSO}_4][\text{SO}_4^{2-}] / [\text{M(SO}_4)_2^{2-}]$$

(6)

it can be shown that

$$\varphi = 2m_s - \Sigma m_i/(\Sigma m_i - m_s)^2 = 1/k_1 + \Sigma m_i/k_1k_2$$

(7)

Replacement of $\Sigma m_i$ by $\Sigma \overline{m}_i$ obtained from measurements according to eqn. (2) gives an approximate value $\overline{\varphi}$ for $\varphi$. The value of $\overline{\varphi}$ equals the value of $\varphi$ when extrapolated to infinite dilution of the added electrolyte, as can be seen from eqns. (3) and (7). For the electrolytes studied in this investigation the variation of $\overline{\varphi}$ with $\Sigma \overline{m}_i$ in all cases is linear within the limits of the experimental error. The intercept of these lines on the $y$-axis gives the value $\overline{\varphi} = 1/k_1$. The slope of these lines gives at most only a rough approximation for $1/k_1 k_2$ due to the changes in activity coefficient. In addition the ions of the saturating electrolyte may also participate in ion-pair formation. The effect of this on $\overline{\varphi}$ can be assumed to be slight. It may be pointed out that the same method could be applied using pure water as a solvent but the variation of $\overline{\varphi}$ with $\Sigma \overline{m}_i$ would not be linear, and here again some arbitrary assumptions about the ion activities would be necessary for the extrapolation of $1/k_1$. The method will, of course, give classical dissociation constants at the ionic strength of the saturating electrolyte.

RESULTS

The author has previously studied the ion association of cupric sulphate, zinc sulphate, nickel sulphate and magnesium sulphate in saturated potassium perchlorate solutions. The same dissociation constants have now been determined in saturated potassium chlorate and potassium nitrate solutions. The freezing point depressions were measured using the method of Richards. The apparatus used, consisting of two Dewar vessels, propeller driven water circulator and ten-junction thermocouples, and the method have been described previously. The accuracy in temperature measurements was about 0.0003°C. The concentrations of copper, zinc, nickel and magnesium were determined by complexometric methods. All reagents were of A.R. grade.

The molar depressions of the eutectic points of these solutions in equilibrium with ice were determined using nitric acid in the case of potassium chlorate and hydrochloric acid in the case of potassium nitrate. As before, an empirical equation

$$K_t \equiv \Delta T/2m_a = K^\circ_t + a \cdot m_a$$

was found suitable for the extrapolation of $K^\circ_t$ values. The following equations were derived using the method of least squares:

$$K_t = 1.803 - 0.106 \, m_{\text{HNO}_3}$$

for potassium chlorate solutions and

$$K_t = 1.693 - 0.141 \, m_{\text{HCl}}$$

for potassium nitrate solutions. All concentrations are expressed in moles per kg of water. The eutectic point for saturated potassium chlorate solution in equilibrium with ice was found to be $-0.800^\circ$C and the saturation concentration at this temperature was 0.258 molal, for saturated potassium nitrate solution these values were $-2.831^\circ$C and 1.150 moles per kg of water, respecti-
\textit{Tables 1 and 2.} Eutectic point depressions for saturated potassium chloride (1) and potassium nitrate (2) solutions produced by various sulphates and dissociation constants calculated from these data.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
$m_*$ & $\Delta T$ & $\Sigma \bar{m}_i$ & $\overline{\varphi}$ & $k_1$ \\
\hline
CuSO$_4$ &  &  &  & \\
0.0221 & 0.0681 & 0.0378 & 26.0 & 0.051 \\
0.0433 & 0.1222 & 0.0678 & 31.3 & \\
0.0641 & 0.1695 & 0.0940 & 38.3 & \\
0.0837 & 0.2142 & 0.1188 & 39.4 & \\
0.1027 & 0.2566 & 0.1423 & 40.2 & \\
0.1210 & 0.2919 & 0.1619 & 47.9 & \\
0.1386 & 0.3267 & 0.1812 & 52.9 & \\
\hline
ZnSO$_4$ &  &  &  & \\
0.0330 & 0.0977 & 0.0542 & 26.3 & 0.049 \\
0.0655 & 0.1788 & 0.0922 & 28.0 & \\
0.0954 & 0.2467 & 0.1368 & 31.5 & \\
0.1247 & 0.3075 & 0.1707 & 37.3 & \\
0.1457 & 0.3548 & 0.1968 & 36.2 & \\
0.1730 & 0.4078 & 0.2262 & 42.3 & \\
\hline
NiSO$_4$ &  &  &  & \\
0.0213 & 0.0660 & 0.0366 & 25.6 & 0.054 \\
0.0418 & 0.1185 & 0.0657 & 31.3 & \\
0.0618 & 0.1658 & 0.0920 & 34.6 & \\
0.0816 & 0.2087 & 0.1157 & 40.8 & \\
0.1003 & 0.2470 & 0.1370 & 47.2 & \\
0.1173 & 0.2846 & 0.1578 & 46.8 & \\
0.1364 & 0.3210 & 0.1780 & 54.8 & \\
\hline
MgSO$_4$ &  &  &  & \\
0.0286 & 0.0905 & 0.0502 & 15.0 & 0.087 \\
0.0569 & 0.1632 & 0.0905 & 20.6 & \\
0.0820 & 0.2251 & 0.1248 & 21.4 & \\
0.1083 & 0.2839 & 0.1575 & 24.4 & \\
0.1332 & 0.3379 & 0.1874 & 26.9 & \\
0.1565 & 0.3878 & 0.2151 & 28.5 & \\
0.1797 & 0.4354 & 0.2415 & 30.9 & \\
\hline
\end{tabular}
\end{table}

The results of measurements made with the different sulphates are given in Tables 1 and 2. These gave the expressions

\begin{align}
\overline{\varphi}_{\text{CuSO}_4} &= 18.5 + 185\Sigma \bar{m}_i \\
\overline{\varphi}_{\text{ZnSO}_4} &= 21.0 + 85\Sigma \bar{m}_i \\
\overline{\varphi}_{\text{NiSO}_4} &= 18.5 + 190\Sigma \bar{m}_i \\
\overline{\varphi}_{\text{MgSO}_4} &= 11.7 + 80\Sigma \bar{m}_i
\end{align}

for saturated potassium chloride solutions and

\begin{align}
\overline{\varphi}_{\text{CuSO}_4} &= 5.3 + 31\Sigma \bar{m}_i \\
\overline{\varphi}_{\text{ZnSO}_4} &= 4.6 + 36\Sigma \bar{m}_i \\
\overline{\varphi}_{\text{NiSO}_4} &= 4.9 + 34\Sigma \bar{m}_i \\
\overline{\varphi}_{\text{MgSO}_4} &= 2.4 + 15\Sigma \bar{m}_i
\end{align}

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for saturated potassium nitrate solutions. For saturated potassium perchlorate solutions the author earlier obtained the equations:

\[
\begin{align*}
\bar{\varphi}_{\text{CuSO}_4} &= 49.3 + 359\bar{\Sigma}m_i \\
\bar{\varphi}_{\text{ZnSO}_4} &= 51.1 + 238\bar{\Sigma}m_i \\
\bar{\varphi}_{\text{NiSO}_4} &= 50.5 + 161\bar{\Sigma}m_i \\
\bar{\varphi}_{\text{MgSO}_4} &= 36.3 + 157\bar{\Sigma}m_i \\
\end{align*}
\]

In all cases the variation of \( \varphi \) with \( \bar{\Sigma}m_i \) is linear within the limits of experimental error. This is an empirical assumption, and much more accurate measurements are required to show whether it is really valid. In any case the relationship between \( \bar{\varphi} \) and \( \Sigma m_i \) is so nearly linear that even where it is more complicated the linear extrapolation will not lead to any large error in \( k_1 \). There can hardly be any unexpected variations in \( \bar{\varphi} \) between the points of intersection and the first points measured at such relatively high ionic strengths. The variations in the values of \( k_1 \) obtained from eqns. (11), (12)
and (13) with ionic strength have been expressed by means of the Debye-Hückel equation

\[ pk_1 = pk_1^0 - 3.9 \sqrt{I}/(1 + a\sqrt{I}) + BI \]  

(14)

The values obtained for \( pk_1^0 \), \( a \) and \( B \) and the values of \( pk_1 \) at different ionic strengths are shown in Table 3. The values of \( k_1 \) for each ionic strength were measured at several temperatures for solutions of different saturating electrolytes and, strictly speaking, eqn. (14) is not applicable as such to the experiments. The effect of the temperature on \( k_1 \) can be estimated according to the Bjerrum theory of ion-pair formation\(^8\). For instance, for the \( pk_1 \) value 2.300 at 0°C this gives a theoretical value of 2.293 at −3°C. The effects of temperature differences are, therefore probably within the limits of the experimental error and have been ignored. The characteristic salt effects of the different saturating electrolytes on the \( pk_1 \) values can similarly be assumed to be negligible. The dissociation constants for these sulphates have been reported frequently before \(^9\)–\(^14\). Although the values obtained depend on various assumptions on activity factors of ions, they agree, being mostly of a magnitude of 0.003—0.008, remarkably well with each other and the values in Table 3. Näsänen\(^15\) has obtained spectrophotometrically for cupric sulphate

\[ pk_1 = 2.099 - 4.05 \sqrt{I}/(1 + 1.618 \sqrt{I}) + 0.0521I \]  

(15)

Table 3. Values of \( pk_1 \), \( pk_1^0 \), \( a \), and \( B \) for some bivalent metal sulphates.

<table>
<thead>
<tr>
<th>( pk_1 )</th>
<th>( pk_1^0 )</th>
<th>( V \sqrt{I} )</th>
<th>( CuSO_4 )</th>
<th>( ZnSO_4 )</th>
<th>( NiSO_4 )</th>
<th>( MgSO_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO(_3) sol.</td>
<td>-2.831</td>
<td>1.073</td>
<td>0.724</td>
<td>0.663</td>
<td>0.690</td>
<td>0.380</td>
</tr>
<tr>
<td>KClO(_3) sol.</td>
<td>-0.800</td>
<td>0.508</td>
<td>1.290</td>
<td>1.312</td>
<td>1.267</td>
<td>1.061</td>
</tr>
<tr>
<td>KClO(_4) sol.</td>
<td>-0.163</td>
<td>0.220</td>
<td>1.692</td>
<td>1.708</td>
<td>1.703</td>
<td>1.561</td>
</tr>
<tr>
<td>( pk_1^0 ), water</td>
<td>0.000</td>
<td>0.000</td>
<td>2.259</td>
<td>2.256</td>
<td>2.294</td>
<td>2.186</td>
</tr>
<tr>
<td>( a )</td>
<td>-</td>
<td>-</td>
<td>2.55</td>
<td>2.90</td>
<td>2.22</td>
<td>1.87</td>
</tr>
<tr>
<td>( B )</td>
<td>-</td>
<td>-</td>
<td>-0.36</td>
<td>-0.50</td>
<td>-0.32</td>
<td>-0.36</td>
</tr>
</tbody>
</table>

According to this the variation of \( pk_1 \) values with ionic strength is similar to that obtained by the author at low values of ionic strength. At higher ionic strengths some differences appear due to the abnormally large \( B \)-values obtained in this work. The fact that the optical method of Näsänen gives values for \( k_1 \) about one and a half times as large as those given by e.m.f., conductance and cryoscopic methods\(^16\) raises again the question whether all such ion-pairs formed by electrostatic forces, which can be detected by the latter methods, undergo any changes in optical properties. For cupric sulphate Fronaús\(^17\),\(^18\) obtained spectrophotometrically \( k_1 = 0.2 \) and potentiometrically \( k_1 = 0.1 \) at \( I = 1 \). The former value is in excellent agreement with the corresponding value, \( k_1 = 0.200 \), obtained in this paper.

REFERENCES


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