Conductometric study of ion-pair formation in aqueous solutions of potassium pyrosulphate at different temperatures

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The thermodynamic association constant \( (K_a) \) for \( K_2S_2O_7^- \) ion-pair has been determined at four different temperatures, e.g. 298.15, 303.15, 308.15 and 313.15 K, in aqueous medium using Shedlovsky and Fuoss-Kraus extrapolation techniques. The thermodynamic functions for the process of ion-pair formation have been evaluated and discussed.

In continuation of our study on the determination of association parameters \( (\Lambda_0 \text{ and } K_a) \) of a number of 1:1 and 1:2 electrolytes in aqueous and different aquo-organic solvent systems from conductance data, the present work aims at determining the conductivity values of potassium pyrosulphate in water at 298.15, 303.15, 308.15 and 313.15 K to examine the validity of Shedlovsky and Fuoss-Kraus conductance equations in evaluating the association parameters in aqueous medium. The thermodynamic parameters for the process of ion-pair formation have been evaluated.

**Experimental**

Potassium pyrosulphate (E. Merck) of GR grade was used as such. Conductivity water \( (\kappa = 1 \times 10^{-6} \text{S cm}^{-1}) \) was used for preparing potassium pyrosulphate solutions. Conductance measurements were made on a digital reading conductivity meter (Systronics, Type 304) with a sensitivity of 0.1% and a dipping type conductivity cell with platinumized electrodes (cell constant, 1 S cm\(^{-1}\)). The experiment was repeated several times with different concentrations of potassium pyrosulphate. All measurements were carried out in water thermostat maintained at appropriate temperatures varying within ±0.05 K. The conductivities of salt solutions were always corrected for the contribution of the solvent (e.g. water) conductivity.

**Results and discussion**

The values of molar conductivity, \( \Lambda \) at any molar concentration, \( c \) (mol dm\(^{-3}\)) have been computed from the corrected conductivity data. An auxiliary function, \( \Lambda' \) was calculated using the relation:

\[
\Lambda' = (\Lambda + A d^{1/2})/(1 - B c^{1/2}) \quad \ldots (1)
\]

where \( A \) and \( B \) are the Onsager constants and were estimated by means of usual equations and by using the values of viscosity and dielectric constant of water at 298.15, 303.15, 308.15 and 313.15 K available in the literature.

Approximate value of molar conductivity at infinite dilution \( \Lambda_0 \text{ (approx)} \) was obtained by linear extrapolation of the auxiliary function \( \Lambda' \) as a function of \( c^{1/2} \),

\[
\Lambda' = \Lambda_0 \text{ (approx)} - S c^{1/2} \quad \ldots (2)
\]

where \( S \) is the Onsagor slope. This value of \( \Lambda_0 \text{ (approx)} \) was used to determine the Onsagor slope \( S \) as follows:

\[
S = 82.4 \left( DT^{1/2} \eta^{-1} + 8.20 \times 10^5 \right) \Lambda_0 \text{ (approx)} \quad \ldots (3)
\]

where \( D \) is the dielectric constant of water, \( \eta \) is the coefficient of viscosity and \( T \) is the temperature. Using the values of \( D \) and \( \eta \) of water available in literature at different temperatures, the value of \( S \) was estimated by Eq. (3).

Using these \( S \) and \( \Lambda_0 \text{ (approx)} \) values, \( Z, S(z) \) and \( a \) (the degree of dissociation) values were calculated by the following equations.

\[
Z = S(\kappa C)^{1/2}/\Lambda_0^{1/2} \quad \ldots (4)
\]

\[
S(z) = 1 + Z + Z^2/2 + Z^3/8 \quad \ldots (5)
\]
CONDUCTOMETRIC STUDY OF ION-PAIR FORMATION IN AQ. K$_2$S$_2$O$_7$

Table I—Values of the limiting molar conductivity, $\Lambda_\infty$ (S cm$^{-2}$ mol$^{-1}$) for K$_2$S$_2$O$_7$ in water at different temperatures

<table>
<thead>
<tr>
<th>T(K)</th>
<th>S-technique F-technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Lambda_\infty = 0$</td>
</tr>
<tr>
<td>298.15</td>
<td>812.73 ± 40.18</td>
</tr>
<tr>
<td>303.15</td>
<td>867.65 ± 44.56</td>
</tr>
<tr>
<td>308.15</td>
<td>921.88 ± 48.80</td>
</tr>
<tr>
<td>313.15</td>
<td>978.86 ± 53.38</td>
</tr>
</tbody>
</table>

Table 2—Values of $K_a$ (dm$^3$ mol$^{-1}$) of K$_2$S$_2$O$_7$ ion-pair in water at different temperatures

<table>
<thead>
<tr>
<th>T(K)</th>
<th>S-technique F-technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a\Lambda S(z)/\Lambda_0$</td>
</tr>
<tr>
<td>298.15</td>
<td>47.58 ± 4.86</td>
</tr>
<tr>
<td>303.15</td>
<td>51.49 ± 5.28</td>
</tr>
<tr>
<td>308.15</td>
<td>54.96 ± 5.82</td>
</tr>
<tr>
<td>313.15</td>
<td>58.75 ± 6.40</td>
</tr>
</tbody>
</table>

\[ a = \Lambda S(z)/\Lambda_0 \]  \( \ldots (6) \)

where $\Lambda$ and $\Lambda_0$ in Eqs (4) and (6) are $\Lambda'$ and $\Lambda_0$ (approx) respectively.

Using this $a$ value and the value $D$, the dielectric constant of water obtained from the literature at different temperatures, the values of $\lambda_\pm$, the mean ionic activity co-efficient were evaluated by means of Eq. (7)

\[ 1.824 \times 10^6 z_+ z_- \left(DT\right)^{-2} \left[1 + (2a) \right] \frac{c^2}{2} 
\log f_z = \frac{1}{1 + a^2 \frac{50.29}{10^6 \left(DT\right)^{-1}} \left(1 + 2a\right)^2} \]  \( \ldots (7) \)

with $a^0$ (the distance of closest approach of ions) = 0, $q$ and $2q$, where $z_+$ and $z_-$ are ion valencies and $q$ is the Bjerrum critical distance and equals $z_+ \cdot z_- e^2/2DKT$ (the symbols have their usual meanings).

Using these initial values of $S(z)$ and $f_z$ (for $a^0 = 0$, $q$ and $2q$ separately) and of $\Lambda$ (i.e. $\Lambda'$ as obtained by Eq. (1)), the values of $1/\Lambda S(z)$ and $c\Lambda f_z S(z)$ were calculated and plotted according to the following equation\(^4\) (i.e. Shedlovsky extrapolation technique)

\[ \frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \left(\frac{K_a}{\Lambda_0}\right) f_z S(z) \]  \( \ldots (8) \)

to get $\Lambda_0$ and $K_a$ values from the intercept and slope, respectively. Using this new value of $\Lambda_0$ the values of $S$, $\Lambda$ (i.e. $\Lambda'$ using Eq. (2)) and $f_z$ (with $a^0 = 0$, $q$ and $2q$), $Z$, $S(z)$, and $a$ were further evaluated. The values of $1/\Lambda S(z)$ and $c\Lambda f_z S(z)$ were again calculated and plotted according to Eq. (8) to yield better values of $\Lambda_0$ and $K_a$. The procedure was repeated using the new value of $\Lambda_0$ till the constancy in $\Lambda_0$ and $K_a$ values appeared.

The conductance data were also analysed using the Fuoss-Kraus extrapolation technique\(^5\)

\[ F(z)/\Lambda = 1/\Lambda_0 + (K_a/\Lambda_0) (c\Lambda f_z S(z)) \]  \( \ldots (9) \)

where

\[ F(z) = (4/3) \cos^3[(1/3) \cos^{-1}(1/3)] \]

\[ a = \Lambda/\Lambda_0 \]

and $Z$ and $f_z$ were the same as defined in Eqs (4) and (7) respectively. The values of $\Lambda_0$ and $K_a$ were estimated by following the iteration process similar to that described in the case of Shedlovsky technique.

All the calculations were carried out on PC-386-DX computer, and the results are shown in Tables 1 and 2, along with standard deviations.

The values of $\Lambda_0$ obtained for K$_2$S$_2$O$_7$ and that of $pK_a$ for K$_2$S$_2$O$_7$ ion pair in association equilibrium $K^+ + S_2O_7^{2-} \rightarrow K_2S_2O_7$ at the four different temperatures using both the Shedlovsky (S) and Fuoss-Kraus (FK) techniques were fitted by least-squares method to equations of the type\(^6\),

\[ \Lambda_0 = a + bT \]  \( \ldots (10) \)
Table 3—Values of the parameters \( a \) and \( b \) for \( \Lambda_0 \) and \( A, B \) and \( C \) for \( pK_A \) in water

<table>
<thead>
<tr>
<th>( a ) ( b \times 10^3 )</th>
<th>( A )</th>
<th>( B \times 10^4 )</th>
<th>( C \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a ) ( =q ) ( =2q )</td>
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<tr>
<td>( \pm 0.7421 ) ( \pm 0.7252 ) ( \pm 0.7145 )</td>
<td>( \pm 0.7391 ) ( \pm 0.7268 ) ( \pm 0.7143 )</td>
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<tr>
<td>( \pm 2.4050 ) ( \pm 2.3496 ) ( \pm 2.3146 )</td>
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<tr>
<td>( \pm 1505.0382 ) ( \pm 1533.6111 ) ( \pm 1505.0382 )</td>
<td>( \pm 1504.4883 ) ( \pm 1533.6111 ) ( \pm 1505.0382 )</td>
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<td>( \pm 1504.4883 ) ( \pm 1533.6111 ) ( \pm 1505.0382 )</td>
</tr>
</tbody>
</table>

Table 4—Thermodynamic quantities for \( KS_2O_4^- \) ion-pairs in aqueous medium at 298.15 K

<table>
<thead>
<tr>
<th>( a ) ( b \times 10^3 )</th>
<th>( A )</th>
<th>( B \times 10^4 )</th>
<th>( C \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta G^0 ) ( \text{(kJ mol}^{-1} )</td>
<td>( \Delta H^0 ) ( \text{(kJ mol}^{-1} )</td>
<td>( \Delta S^0 ) ( \text{(J mol}^{-1}K^{-1} )</td>
<td>( \Delta C_p^{\text{aq}} \times 10^2 ) ( \text{(kJ mol}^{-1}K^{-1} )</td>
</tr>
<tr>
<td>( \pm 9.57 \pm 0.25 \pm 9.44 \pm 0.25 \pm 9.36 \pm 0.25 )</td>
<td>( \pm 10.30 \pm 0.50 \pm 10.19 \pm 0.50 \pm 10.13 \pm 0.50 )</td>
<td>( \pm 67 \pm 3 \pm 66 \pm 3 \pm 65 \pm 3 )</td>
<td>( \pm 6.91 \pm 0.33 \pm 6.84 \pm 0.33 \pm 6.80 \pm 0.33 )</td>
</tr>
</tbody>
</table>

\( pK_A = AT + B + CT \) ... (11)

respectively where \( T \) is the temperature. The parameters \( a \) and \( b \) for \( \Lambda_0 \) and \( A, B \) and \( C \) for \( pK_A \) are recorded in Table 3 along with their standard deviations.

The various thermodynamic parameters for the association process of \( KS_2O_4^- \) ion pair in their standard states have been evaluated by means of usual relations and are given in Table 4 for 298.15 K only.

A perusal of Table 1 shows that the values of \( \Lambda_0 \) derived from both S and FK techniques with \( a = q \) and \( 2q \) for calculating activity coefficient are very close to each other.

Association constants \( (K_A) \) estimated from S and FK techniques taking \( a^0 = 0 \) and \( 2q \) are recorded in Table 2. Our investigations of potassium pyrosulphate show a considerable ion pair formation. Of such cases deviations from the limiting Onsager and Debye-Hückel equations can be attributed almost wholly to the strong cation-anion electrostatic interaction.

A perusal of Table 4 shows that the \( \Delta H^0 \) and \( \Delta S^0 \) values for the association process are positive. The more positive value for \( \Delta S^0 \) indicates that the ions are hydrated. As observed, the standard change in heat capacity, \( \Delta C_p^0 \) for the association process is positive. Electrostatic interactions between ions and dipolar solvent molecules (e.g. water) would be expected to change the entropy and heat capacity of the system in the same direction, which is found to be in accord with our actual observations.

References