The Conductance of Sodium Perchlorate in Water-sulfolane Mixtures at 35 °C

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Measurements on the conductance of dilute solutions of sodium perchlorate, at 35 °C, in water-sulfolane mixtures over the entire solvent composition range are reported. Experimental data were analyzed by the 1965 Fuoss-Onsager-Skinner equations.

No detectable ion association was found for this electrolyte, unlike sodium chloride in the same solvent mixtures. The association order $K_A(\text{Cl}^-) > K_A(\text{ClO}_4^-)$ is in contrast with that observed in protic solvents [$K_A(\text{ClO}_4^-) > K_A(\text{Cl}^-)$] and is similar to that found in aprotic solvents. This shows that in water-sulfolane mixtures, association phenomena are mainly controlled by sulfolane.

The lack of transport numbers for water-sulfolane mixtures precludes unambiguous explanations for Walden products $\Lambda_6 \eta$.

Introduction

Earlier studies from this laboratory indicate that the ion association of lithium $^1$, sodium $^2$ and potassium $^3$ chlorides in water-sulfolane mixtures is higher than expected on the basis of simple electrostatic theory. Association constants, higher than the Fuoss $^4$ and Bjerrum $^5$ equations predict, were also found in several protic solvents by Evans and co-workers $^6$ and they offered a satisfactory explanation by discussing this anomalous behaviour in terms of a multiple-step association process. The proposed mechanism predicts that perchlorates are more associated than chlorides.

With the purpose of seeing if this association trend also holds good in mixtures of protic with aprotic solvents like water-sulfolane, the conductance of sodium perchlorate was measured in these mixtures over the entire 0 – 100% sulfolane composition range at 35 °C.

Experimental

Water and sulfolane purification has already been described $^7$.

Sodium perchlorate (Fisher Scientific Company) was recrystallized three times from conductivity water and dried under vacuum at 150 °C.

Conductance cells were of the Erlenmeyer type as described by Daggett, Bair and Kraus $^8$. Their constants were determined at 25 °C by measuring the conductance of aqueous potassium chloride solutions.

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Results

The properties of the solvent mixtures are summarized in Table 1. The symbols have the following meanings: $w_2$ and $N_2$ are sulfolane weight per cent
Table 1. Properties of water-sulfolane mixtures at 35 °C.

<table>
<thead>
<tr>
<th>System</th>
<th>( w_2 )</th>
<th>( N_2 )</th>
<th>( q ) (g/ml)</th>
<th>( \eta ) (cP)</th>
<th>( D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>0.99046</td>
<td>0.7194</td>
<td>74.64</td>
</tr>
<tr>
<td>2</td>
<td>12.135</td>
<td>0.02052</td>
<td>1.02176</td>
<td>0.8287</td>
<td>72.30</td>
</tr>
<tr>
<td>3</td>
<td>34.257</td>
<td>0.07309</td>
<td>1.07499</td>
<td>1.1445</td>
<td>67.24</td>
</tr>
<tr>
<td>4</td>
<td>55.464</td>
<td>0.1589</td>
<td>1.12893</td>
<td>1.6577</td>
<td>61.47</td>
</tr>
<tr>
<td>5</td>
<td>74.053</td>
<td>0.3050</td>
<td>1.17932</td>
<td>2.5445</td>
<td>55.09</td>
</tr>
<tr>
<td>6</td>
<td>91.286</td>
<td>0.6111</td>
<td>1.22913</td>
<td>4.4414</td>
<td>47.57</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>1.0000</td>
<td>1.25752</td>
<td>9.033</td>
<td>42.71</td>
</tr>
</tbody>
</table>

and mole fraction; \( q, \eta \) and \( D \) are densities, viscosities and dielectric constants of the solvents.

Table 2 gives equivalent conductances \( A \) and concentrations \( c \) for sodium perchlorate in the different systems which are identified by their dielectric constants. The experimental data were analyzed using the Fuoss-Onsager-Skinner equations, for associated (1) and unassociated (2) electrolytes:

\[
A = A_0 - S c \gamma + E c \gamma \ln \gamma + L c \gamma
- Kc \gamma A \exp ( - 2 \gamma ),
\]

\[
A = A_0 - S c \gamma + E c \gamma \ln \gamma + L c.
\]

All calculations were performed on an IBM 360/65 computer using the Skinner and Fuoss program. Analysis by Eq. (1) gave for all studied systems negative association constants or very small \( K \) values with standard deviations larger than \( K \). Then, the data were automatically processed by the two-parameters Equation (2).

Table 2. Equivalent conductance of sodium perchlorate in water-sulfolane mixtures at 35 °C.

<table>
<thead>
<tr>
<th>System</th>
<th>( A )</th>
<th>( A \cdot 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.779</td>
<td>138.03 + 10</td>
</tr>
<tr>
<td>2</td>
<td>24.314</td>
<td>136.90 + 12</td>
</tr>
<tr>
<td>3</td>
<td>34.839</td>
<td>135.89 - 17</td>
</tr>
<tr>
<td>4</td>
<td>42.575</td>
<td>135.28 - 10</td>
</tr>
<tr>
<td>5</td>
<td>50.595</td>
<td>134.69 - 27</td>
</tr>
<tr>
<td>6</td>
<td>57.964</td>
<td>134.22 - 17</td>
</tr>
<tr>
<td>7</td>
<td>64.910</td>
<td>133.84 + 23</td>
</tr>
<tr>
<td>8</td>
<td>75.204</td>
<td>133.26 + 17</td>
</tr>
</tbody>
</table>

Discussion

Sodium perchlorate does not appear appreciably associated to ion pairs over the entire solvent composition range. On the contrary, previous measurements have shown that sodium chloride in the same solvent mixtures is associated starting from \( w_2 \geq 70 \) wt% sulfolane (\( D \geq 55 \)). Hence in water-sulfolane sodium chloride is more associated than sodium perchlorate. This association order agrees with that observed in pure sulfolane and in other aprotic solvents like acetone, nitrobenzene, nitromethane, acetonitrile, 1,1,3,3 tetramethyl...
urea. It is, on the contrary, the opposite of what is observed in protic solvents where perchlorates are more associated than chlorides.

The association behaviour found in the latter solvents has been interpreted by Evans et al. supposing that the association mechanism for a salt MX in a protic solvent SH is a multiple-step process according to the equations:

\[
M^+ + X^- (SH)_n \leftrightarrow M^+ (SH)_n X^- ,
\]

\[
M^+(SH)_n X^- \leftrightarrow M^+ X^- (SH)_{n-1} + (SH) .
\]

Equation (3) predicts the formation of a "solvent-separated ion pair", which rearranges to a "contact ion pair", by losing a solvent molecule as shown in Equation (4).

The experimental association constant is:

\[
K_A = K_1 (1 + K_2 / [SH])
\]

where \(K_1\) may be calculated from the Fuoss equation and \(K_2\) depends on the strength of anion solvation. Equation (5) accounts for association constants higher than expected on the basis of electrostatics (\(K_A > K_1\)). Furthermore, as expected on the basis of ionic radii, \(K_2\) is greater for perchlorates than chlorides and this accounts for the observed association behaviour in protic solvents.

In aprotic solvents anions are scarcely solvated; therefore chloride is more associated than perchlorate because the former interacts more strongly with cations, having a higher charge density than the latter.

In water-sulfolane mixtures the sodium chloride association, greater than expected on the basis of the Fuoss equation, could be accounted for by the mechanism suggested by Evans and co-workers, assuming that anions, which form ion pairs, are preferentially solvated by water. In this case sodium perchlorate should be more associated than chloride. However the order observed, typical of aprotic solvents, shows that association phenomena in our mixtures depend on the fraction of ions interacting with sulfolane. Heat of transfer data show that the chloride ion is less stabilized in sulfolane than in protic solvents. Thus it forms very stable ion pairs in sulfolane, as shown by the high value of the association constant for LiCl (\(K_A = 14595\)). The conclusion which can be drawn is that the ions interacting with sulfolane form very stable ion pairs even in water-sulfolane mixtures, in spite of the high value of dielectric constants.

![Fig. 1. Walden products for NaClO₄, at 35 °C, vs. sulfolane mole fraction in solvent mixtures.](image)

Let us now consider the Walden products. Figure 1 shows a minimum in water-rich mixtures followed by a maximum at about 90 wt% sulfolane. It should be possible to find some explanation for this complex trend in terms of structural changes of solvent mixtures or changes of ion solvation on adding sulfolane to water. Nevertheless, we believe that it is necessary to know the ionic contribution to the total \(\Lambda_0\) products, as also shown by Kay, Cunningham and Evans. Unfortunately, the lack of transport numbers for the water-sulfolane mixtures precludes a correct interpretation.

14 C. R. Witschonke and C. A. Kraus, J. Amer. Chem. Soc. 69, 2472 [1947].
18 A. J. Parker, Chem. Rev. 69, 1 [1969].