from the conductance data. So the $\Delta_{\text{W}}$ values of the $\text{R}_4\text{N}^+$ and $\text{Li}^+$, $\text{Na}^+$, $\text{K}^+$, $\text{Rb}^+$, $\text{Cs}^+$, $\text{Br}^+$ and $\text{I}^-$, at different temperatures, were obtained from the limiting ionic conductivity values given in Table 1. The values of viscosity, $\eta$, of the solvent were 2.480 (ref. 3), 2.248, 2.050, 1.871 and 1.705 centipoise ($\pm 0.2\%$) at 25°, 30°, 35°, 40° and 45° respectively and were obtained, except that at 25°, in the laboratory. The plots of $\eta^2$ of $\text{R}_4\text{N}^+$ and $\text{Li}^+$ against temperatures are given in Fig. 1 from which it may be noted that the Walden product for different ions is almost independent of temperature. This indicates that these ions neither break nor promote the structure of the solvent within the temperature range studied presently, apparently because no hydrogen bond structure is present originally in the pure solvent$^1$. It appears that the temperature dependence of the Walden product is not very useful in the study of ion-solvent interaction in non-hydrogen bonded solvents.

A better insight about the ion-solvent interaction can be obtained if the relative positions of the $\Delta_{\text{W}}$ versus temperature curves for different ions, given in Fig. 1, are compared. It may be noted that for $\text{R}_4\text{N}^+$ ions, the Walden product is larger, the smaller the size of the ion. This indicates that the electrostatic ion-solvent interaction, if at all, is very weak in these cases so that the smaller the ion, the faster its movement and the larger the Walden product. The same appears to be true for $\text{Cl}^-$, $\text{Br}^-$ and $\text{I}^-$ ions as well. However, reverse is the case with the common cations which are comparatively much smaller as compared to the $\text{R}_4\text{N}^+$ ions. In these cases, Walden product decreases with the decrease in the radius of the cation. This clearly indicates the role of electrostatic charge density on the ion in inducing strong ion-solvent interaction and solvation. The smaller the ion, the greater the electrostatic charge density on the ion, and stronger the ion-solvent dipole interaction, resulting in a larger size of the solvodynamic unit so that the size of the solvated common cations in propylene carbonate solution is in the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, in spite of the radii of these ions being in the reverse order. These common cations exhibit a similar behaviour in N-methylacetamide and N-methylformamide.

It thus appears that during migration the common cations which are fairly small are covered with a sheath of the solvent molecules. However $\text{R}_4\text{N}^+$ and halide ions move more or less as single and bare ions in propylene carbonate. Further, the solvation of ions is not appreciably affected by temperature within the range studied here.

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References


Conductance of Hydrogen Halides in Diethylene Glycol at Different Temperatures

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Conductance data on hydrogen chloride and hydrogen bromide in diethylene glycol in the temperature range 25-45°C are reported. Further, the temperature coefficient of conductance and the Walden product in this temperature range are presented and it was shown by the application of 1965 Fuoss-Onsager three-parameter equation, that no significant association of the halides occurs in this solvent.

CONDUCTANCE studies on hydrogen halides in non-aqueous solvents, especially the amphi-protic solvents, have received considerable attention.$^1$

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But relatively few data have been analysed in terms of the recent Fuoss-Onsager conductance equation for possible existence of ion association of the halides in these media and practically no such analysis has been reported, so far, in glycols. The present work, which is in continuation of our earlier conductance studies on hydrogen chloride in ethylene and propylene glycols, therefore, deals with the conductance behaviour of hydrogen chloride and hydrogen bromide in diethylene glycol in the temperature range 25–45 °C to elicit information on ion association and to understand the nature of solute-solvent interactions involving the halides in this solvent.

The purification of diethylene glycol, details of the experimental set-ups, the method of preparation, purification and standardization of hydrogen chlorides have been described earlier. Hydrogen bromide gas, generated by the action of bromine on tetraline, was passed successively through traps containing tetraline and cone, H₂SO₄ to absorb any traces of bromine and water respectively before being bubbled into the solvent. The standardization of the stock hydrogen bromide solution was done similar to that of HCl. The temperature was generally maintained to within ±0.01 °C by immersing the cell in an oil bath maintained at the desired temperature for sufficiently long time for the attainment of thermal equilibrium.

The conductance results of the two acids at different temperatures are presented in Fig. 1 in the form of \( \Lambda \) versus \( \sqrt{C} \) plots. The plots are seen to be approximately linear in the concentration ranges studied. Since these concentrations lie outside the range of applicability of the limiting Onsager equation, the data (Fig. 1) were analysed by the Fuoss-Onsager three-parameter equation given by

\[
\Lambda = \Lambda_0 - SC^{1/2} + 2EC \gamma \log \left( \frac{\gamma^{1/2}}{2} \right) + LC\gamma - 2\gamma^{1/2}A \quad \ldots(1)
\]

where the various terms have their usual significance. The calculations were performed on an IBM 370 computer and revealed no significant association of either of the halides in the temperature range studied. The data were, hence, analysed by Fuoss-Onsager two-parameter equation given by

\[
\Lambda = \Lambda_0 - SC^{1/2} + 2EC \log \gamma + LC \quad \ldots(2)
\]

where the various terms have been explained elsewhere. The same computer program as above was employed for this purpose and had provision for performing the calculations using Eq. (2) when the association constant, \( K_A \), is less than 10 as obtained from the three-parameter equation. The \( \Lambda_0 \), the ion size parameter, \( a \), and the standard deviation, \( \sigma \), for the two halides obtained in this manner are given in Table 1. The temperature coefficient of conductance given by

\[
\frac{100}{\Lambda_0} \frac{\Delta \Lambda}{\Delta T}
\]

in the temperature ranges 25–35 °C and 35–45 °C and the Walden products at the three temperatures are recorded in Table 2. A further indication of the complete dissociation of these halides in this solvent was obtained by plotting the function, \( \Lambda' \) (given by Eq. 3)

\[
\Lambda' = \Lambda - \Lambda_0 - SC^{1/2} - EC \log C \quad \ldots(3)
\]

against the concentration of the acid for the two halides at the various temperatures and they were found to be linear with no significant curvature. It is seen (Tables 1 and 2) that \( \Lambda_0 \) of both the acids increases with temperature but the temperature coefficients tend to decrease with increase of

<table>
<thead>
<tr>
<th>Table 2 — Temperature Coefficient and Walden Product of Hydrogen Halides in Diethylene Glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
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<tr>
<td></td>
</tr>
<tr>
<td>HCl</td>
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<tr>
<td>HBr</td>
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<tr>
<th>Table 1 — Limiting Equivalent Conductance and Ion Size Parameter for the Hydrogen Halides in Diethylene Glycol at Different Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. °C</td>
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<td></td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>35</td>
</tr>
<tr>
<td>45</td>
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</tbody>
</table>
The positive temperature coefficient for both the acids can be explained on the basis that increase of temperature (a) causes the rupture of hydrogen bonds in the diethylene glycol molecules and (b) will facilitate the rotation of solvent molecules by increasing the force causing the rotation. Thus both the effects increase the mobility of the protons. The ion size parameter obtained for hydrogen chloride is of the same order as in the case of DMSO-water mixtures and is unaffected by temperature changes. The near constancy of the Walden product (Table 2) is most presumably due to the compensating contribution of the acids by the negative temperature coefficient of the viscosity of the solvent. The slight decrease of this quantity with increase in temperature is in agreement with the observations on hydrogen chloride in propanol-water mixtures.

Our sincere thanks are due to Prof. M. Goffredi of the University of Palermo, Italy, for providing us the computer programme which made this work possible. We thank the CSIR, New Delhi, for the award of a senior research fellowship to one of us (V.S.R.).

References

Stability Constants of Chelates of Solochrome

Dark Blue (Calcon) with La(III), Pr(III), Nd(III), Gd(III), Tb(III), Dy(III) & Ho(III)

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The stability constants of 1:1 complexes of solochrome dark blue (calcon) with a few lanthanides have been determined potentiometrically in aq. dioxane (50%, v/v) using the Irving Rossotti titration technique. The compound in view of the hydroxy groups ortho to the azo group form well defined complexes with several metal ions. Complexes of calcon (I) with La(III) were first reported by Rehman et al. In the present note, we have determined the stability constants of the chelates of calcon with other lanthanides in aq. dioxane employing Irving and Rossotti titration technique.

Dioxane was purified by recommended procedure. Carbonate-free sodium hydroxide (E. Merck, 0-4M) was standardized against solid potassium hydrogen phthalate (BDH AnalR). Sodium salt of calcon (BDH) was purified as the corresponding acid by the method of Langmyhr. The purified sample was stored in an anhydrous calcium chloride desiccator.

Solutions of the ligand (0-005M) were obtained by dissolving it in aq. dioxane (50%, v/v) and standardized potentiometrically. Rare earth metal oxides (Indian Rare Earths, Kerala, purity > 99-9%) were used in the form of their nitrates for the preparation of stock metal ion solutions in doubly distilled water. All metal ion stock solutions were 0-00165M in 0-05M perchloric acid (Riedel, Germany) and their metal ion contents were estimated by the gravimetric method.

Systronic pH-meter (type 322-1, accuracy ± 0.05 pH units) using a glass calomel assembly calibrated at the working temperatures was used to measure the apparent pH.

The ligand to metal ratio was kept around 3:1 in all titrations. All experiments were performed at 30°, 40° and 50° and at μ = 0-1 (NaClO4) under oxygen-free nitrogen presaturated with 50% (v/v) aq. dioxane.

As one of the —OH groups of the reagent dissociates at higher pH, the value obtained using the potentiometric method was checked spectrophotometrically. Values of the formation functions nA and pL were calculated using the standard expressions. The values of log K1 and log K2 obtained from the nA versus pH (meter reading) curves were refined by (i) interpolation at half nA values and (ii) interpolation at various nA values. Stability constants

Table 1 — Stability Constants and ΔF of Chelate Formation

<table>
<thead>
<tr>
<th>M**</th>
<th>log K1</th>
<th>ΔF kcal/mole</th>
</tr>
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<tbody>
<tr>
<td>La</td>
<td>9·86</td>
<td>13·67</td>
</tr>
<tr>
<td>Pr</td>
<td>10·47</td>
<td>—</td>
</tr>
<tr>
<td>Nd</td>
<td>10·49</td>
<td>14·54</td>
</tr>
<tr>
<td>Gd</td>
<td>11·52</td>
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<td>Tb</td>
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<tr>
<td>Dy</td>
<td>11·94</td>
<td>16·55</td>
</tr>
<tr>
<td>Ho</td>
<td>12·13</td>
<td>16·82</td>
</tr>
</tbody>
</table>

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