Applicability of Fuoss-Onsager Equation to Electrical Conductances of Dilute Solutions of Triethyl-n-propylammonium Iodide

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The electrical conductances of triethyl-n-propylammonium iodide (Et₃PrNI) recorded in water (dielectric constant, D = 78), nitrobenzene (D = 34), acetic anhydride (D = 20), 1-butanol (D = 17), and benzyl alcohol (D = 13) at 30° have been analysed in terms of Fuoss-Onsager equation. The limiting equivalent conductance, \( \Lambda_0 \), the ion-size parameter, \( a^0 \), and the association constant, \( K_A \), have been computed. The ion-size parameter is found to be independent of the dielectric constant of the medium; the association constants, however, show an exponential relationship whereas walden products show no regular variation. Besides the dielectric constant, the viscosity of the medium has also been found to affect significantly the value of \( \Lambda_0 \).

**Results and Discussion**

The measured equivalent conductances of Et₃PrNI (Table 2) in the solvents under investigation are found to follow the order, \( H_2O > (AcO) > PhNO_2 > BuOH > PhCH₃OH \). The interchanged order in the values of \( \Delta \) in the last two pairs suggests the role of the solvent properties especially the viscosity besides the dielectric constant in determining the magnitude of \( \Delta \) of the added solute. Relatively higher values of conductance for Et₃PrNI in Ac₆O may be ascribed to the dissociation of the solvent molecules which furnish additional ions to the solution.

**Table 1 — Densities and Viscosities (at 30°) of Organic Solvents**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Density (g/cc)</th>
<th>Viscosity (poise)</th>
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<tbody>
<tr>
<td>Nitrobenzene</td>
<td>1.1936</td>
<td>0.0122</td>
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<td>Benzyl alcohol</td>
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**Materials and Methods**

Triethyl-n-propylammonium iodide used was an Eastman Kodak product. All the solvents, benzyl alcohol (PhCH₂OH), 1-butanol (BuOH), acetic anhydride (Ac₂O), nitrobenzene (PhNO₂) and water were distilled and purified before use. The solutions were prepared by weight in a dry box under purified dry \( N_2 \) atmosphere. The conductances (± 0.2%) of dilute solutions of Et₃PrNI were measured at 30° with a conductivity bridge of Philips type PR 9500 at a frequency of 50 Hz. The pyrex conductivity cell (cell constant = 1-0459 cm⁻¹) — Philips type PV 9055 with lightly platinized electrodes was standardized with a decinormal potassium chloride solution at 30° using the constants reported by Lind et al. Density (± 0.3%) and viscosity (± 0.1%) of measurements were made with a calibrated pyknometer of 0.02 ml divisions and a Cannon-Ubbelohde viscometer, respectively. These measurements were made in a relay-controlled thermostated water-bath of ± 0.02° thermal stability. The densities and the viscosities of the organic solvents employed are given in Table 1.

**Table 2 — Densities and Viscosities (at 30°) of Organic Solvents**

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According to Fuoss et al., the long-range interactions between ions not in contact are best described by the equation

\[ A = A_0 - SC^{1/2} + EC \log C + J_0 C \]  

while the short-range interactions which create ion pairs are best described by the equation

\[ A = A_0 - SC^{1/2} + E CY + JCY - K_A CY \]  

where the terms have their usual significances. Recently, "Paracond" has been designed for the para-analysis of conductance data for the symmetrical electrolytes.

In view of the inability of our data to be analysed by the Paracond, Eqs. (1) and (2) were employed for explaining the concentration dependence of the unassociated and the associated electrolytes, respectively. The viscosity correction was not made as \( \Lambda_0 \) and \( K_A \) are found to be unaffected by such a correction while \( \Lambda_0 \) shows a small effect.

The initial values of \( \Lambda_0 \) were obtained from the Fuoss-Shedlovsky extrapolation of the equivalent conductance data by the method of least squares fitting. The \( \Lambda_0 \) values thus obtained were employed in such an analysis. The parameters computed are listed in Table 3.

The computed values of \( \Lambda_0 \) are found to depend on the dielectric constant in a manner similar to those of the equivalent conductances. The single ion conductances (Table 4) of triethyl-n-propylammonium ion in all these solvents were calculated with the help of Walden rule based on the Stoke's law using the crystallographic radii of the iodide ion.

The ionic Walden products, \( \Lambda_{\text{W}} \), have been found to increase with a decrease in the dielectric constant and is consistent with the Fuoss and Zwanzig view. According to them, the dependence of the ionic Walden product on the solvent properties may be given as

\[ \Lambda_{\text{W}} = F^2/N(6\pi r + B/r^2) \]  

where \( B \) is a function of the dielectric constant as well as the viscosity and explains the increase in the ionic Walden product with decreasing dielectric constant. The fact that the values of this product are almost constant in alcohols where the dielectric range is 32-6-17.5 appears to denote that B remains constant in those alcohols.

The Walden product, \( \Lambda_{\text{W}} \), for triethyl-n-propylammonium iodide has been plotted against 1/D (Fig. 1) and a typical variation of \( \Lambda_{\text{W}} \) with dielectric constant of the medium is observed. The plot passes through the maxima corresponding to the dielectric constants of benzyl alcohol and acetic anhydride and through the minima at the dielectric constants of butanol and nitrobenzene. Such a typical behaviour of Walden product may be explained in the light of the limiting equivalent conductance, the viscosity and the dielectric constant of the medium. Mainly, the ion-ion and the ion-solvent interactions play important role in determining the nature of variation in Walden product with the dielectric constant. Therefore, a detailed analysis of such a variation in \( \Lambda_{\text{W}} \) demands a clear insight into the nature of interactions in the system.

The concept of structure making and structure breaking electrolytes suggested by Evans and Kay may be employed for this purpose. In the case of triethyl-n-propylammonium ions possessing large hydrophobic side chains, the solvent molecules may be slightly influenced by the ionic charge of the

### Table 2—Conductance Data of Triethyl-n-Propylammonium Iodide in Several Solvents at 30°C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \Lambda ) (cm² equiv⁻¹ cm⁻¹) at [electrolyte] x 10⁴ (mol/litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100-0</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>100-990</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>26-894</td>
</tr>
<tr>
<td>I-Butanol</td>
<td>49-962</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>3-350</td>
</tr>
</tbody>
</table>

### Table 4—Single Ion Conductivities of Triethyl-n-Propylammonium Iodide and the Ionic Walden Product in Different Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \Lambda_0 )</th>
<th>( \Lambda_{\text{W}} )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>32-86</td>
<td>0-261</td>
<td>0-879</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>25-21</td>
<td>0-307</td>
<td>0-468</td>
</tr>
<tr>
<td>Acetic anhydride</td>
<td>47-21</td>
<td>0-378</td>
<td>0-763</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>13-04</td>
<td>0-613</td>
<td>0-991</td>
</tr>
</tbody>
</table>

The ionic Walden product: \( \Lambda_{\text{W}} \) = 48-11; BuOH = 9-32; PhCH₃OH = 8-04.
unit hydrophobic side chain on the surface of these ions. Hence, the solvent molecule on the hydrophobic surface may be oriented in such a manner as to form a cage about the hydrocarbon side chains. The clathrate thus obtained as a result of solvation increases the size of the entity which in turn decreases the mobility and increases the local viscosity. On this basis the triethyl-n-propylammonium ion is a structure breaker in water, butanol and benzyl alcohol thereby showing abnormality in their Ao'YJ behaviour. The behaviour of log (Ao'/Ao) with change in concentration (Fig. 2) seems to be rather similar to that of the equivalent conductance. This implies that Λ dominates over the viscosity change throughout the concentration range.

The plot of log Kₐ versus 1/D shown in Fig. 3 indicates that the association constant of Et₃PrNI in the solvents under investigation is an exponential function of dielectric constant,

$$K_a = K'_a \exp(\alpha^2/DKt)$$

where the terms have their usual significances. The evaluation of the ion-size parameters using different conductance equations shows a significant difference in the α² values for a definite electrolyte in a particular dielectric medium. For example, the reported values of α² for various tetraalkylammonium salts in ethanol and propanol²⁷ are 4.2 ± 0.2 Å and 5.0 ± 0.5 Å, respectively, and are based on the Fuoss-Onsager equation. Instead, the Fuoss-Hsia²⁰,²¹ analysis of the same data gave comparable but constant values of α² which appeared to be independent of the dielectric constant as is the case with several other solvents²³.²⁴

An examination of Table 3 shows that the ion-size parameter, α² for Et₃PrNI increases from BuOH to PhNO₂. This seems to imply that the ion-pair formation decreases from BuOH to PhNO₂. Moreover, the α² value is found to be small compared to the sum of the crystallographic radii of the cation and the anion. Therefore, the association of Et₃PrN⁺ ion to the solvent molecules may presumably decrease the contact distance parameter. Considering the insignificant influence of the nature of the solvent on the α² values, this quantity may, on the average, be taken as 5.15 ± 1.03 Å in the solvents under discussion.

Acknowledgement

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References

ISLAM et al.: CONDUCTANCE OF $\text{Et}_3\text{PrNI}$ IN DIFFERENT SOLVENTS