Viscosity Studies of Some 1:1 Electrolytes in Ethanolamine at 25°C

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The relative viscosities of LiClO₄, NaBr, NaI, NaNO₃, NaClO₄, NaBPh₄, KBr, KI, and Bu₄NBr have been measured in the concentration range 5.95-106.60 × 10⁻³ mol⁻¹ in ethanolamine at 25°C. The data have been analysed by the Jones-Dole equation; viscosity B coefficients are found to be positive in ethanolamine. Ionic viscosity B-coefficients are obtained by splitting the B-coefficients of Bu₄NBr₄ [B(Bu₄NBr)₄ + B(NaBPh₄)₄ - B(NaBr)₄] into the contributions due to the individual ions in terms of their radii. The solvation behaviour of ions in ethanolamine has been interpreted in terms of the combined equation of Einstein and Jones-Dole.

The viscometric technique has recently been gaining considerable importance in studying the behaviour of electrolytes in pure as well as in mixed solvents. These studies help us to calculate the viscosity B-coefficient of the Jones-Dole equation, which is a useful parameter in interpreting the nature of ion-solvent interactions. In the present study, viscometric measurements are carried out for some 1:1 electrolytes in ethanolamine. The viscosity of ethanolamine is about eight times that of water and the results are expected to throw some light on the solvation of ions in this solvent.

Materials and Methods
Ethanolamine (Sarabhai) was purified by distillation. The distillation was repeated three times and each time middle fraction was collected and was further distilled. The physical properties of the freshly distilled solvent (b.p. = 170-171°C, density = 1.0120 g ml⁻¹, viscosity = 19.342 cP and sp. cond. = 11.5 × 10⁻⁶ ohm⁻¹ cm⁻¹; all at 25°C) agreed well with those reported in literature.

Densities and viscosities were measured by the methods reported earlier.

Results and Discussion
Densities and viscosities of LiClO₄, NaBr, NaI, NaNO₃, NaClO₄, NaBPh₄, KBr, KI and Bu₄NBr have been measured in the concentration range 5.95-106.60 × 10⁻³ mol⁻¹ in ethanolamine at 25°C. The viscosity data have been analysed by using the Jones-Dole equation in the form:

$$\eta/\eta_0 = 1 + AC^1 + BC$$

which may be rearranged as

$$\eta/\eta_0 - 1 = A + BC^1$$

where η and η₀ are the viscosities of the solution and of the pure solvent respectively, C is the molar concentration, and A and B are viscosity coefficients characteristic of the electrolyte and the solvent.

The function $$(\eta/\eta_0 - 1)/C$$ was plotted against C for the different electrolytes in ethanolamine. It was observed that the plots were linear over the whole concentration range studied for all the electrolytes.

The viscosity A coefficients for all the electrolytes in ethanolamine are positive. The B values for the potassium salts are lower than those for the

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>A(1 mol⁻¹)</th>
<th>B(1 mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiClO₄</td>
<td>0.022</td>
<td>1.21</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.021</td>
<td>0.94</td>
</tr>
<tr>
<td>NaI</td>
<td>0.028</td>
<td>0.91</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>0.035</td>
<td>0.88</td>
</tr>
<tr>
<td>NaClO₄</td>
<td>0.032</td>
<td>1.05</td>
</tr>
<tr>
<td>NaBPh₄</td>
<td>0.007</td>
<td>1.75</td>
</tr>
<tr>
<td>KBr</td>
<td>0.028</td>
<td>0.87</td>
</tr>
<tr>
<td>KI</td>
<td>0.003</td>
<td>0.86</td>
</tr>
<tr>
<td>Bu₄NBr</td>
<td>0.013</td>
<td>1.07</td>
</tr>
</tbody>
</table>

† The maximum uncertainty of the B values is ± 0.041 mol⁻¹.
corresponding sodium salts whereas the viscosity $B$ coefficient for NaClO₄ is less than that for LiClO₄.

**Ionic viscosity $B$ coefficients**

There is no experimental method to split viscosity $B$ coefficients into the individual ionic $B$ coefficients, $B_\pm$. Consequently, the division has to be arbitrary and a number of methods have been suggested for doing this by various workers\(^3\). Most of these methods depend upon the choice of a reference salt for which the cation-solvent and anion-solvent interactions may be considered equal.

Recently, Gill and coworkers have suggested\(^{11,12}\) a simple method for splitting $B$ coefficients of electrolytes into the contributions due to the individual ions taking Bu₄NBP₄ as the reference (Eqs 3, 4),

$$\frac{B(Bu_4N^+)}{B(BP_4^-)} = \left(\frac{r(Bu_4N^+)}{r(BP_4^-)}\right)^3$$

$$= \frac{5.00}{5.35}^3 \quad \ldots (3)$$

and

$$B(Bu_4NBp_4) = B(Bu_4N^+) + B(BP_4^-) \quad \ldots (4)$$

This method is based on the assumption that Bu₄N⁺ and BP₄⁻ ions, with large alkyl groups, are not solvated in nonaqueous solvents. However, because of the poor solubility of Bu₄NBp₄ in ethanolamine, the above method could not be applied as such. On the other hand, the solvation of Bu₄NBp₄ in ethanolamine, the value of $B(BP_4^-)$ has been found to be 0.84 and 0.87 respectively. The value of $B(BP_4^-)$ has been used to calculate the ionic $B$-value for Na⁺ by subtracting the $B(BP_4^-)$ from the $B$ value for NaBP₄. This value of Na⁺ ion (0.71 mol⁻¹) has been further used to calculate ionic viscosity $B$ coefficients of all the other ions. The results are recorded in Table 2. The internal accuracy of the experiments has been checked by calculating ionic $B$-values for electrolytes using different anionic or cationic coefficients. For instance, the $B(Br^-)$ values obtained from Bu₄NBBr and NaBr by using $B(Bu_4N^+)$ and $B(Na^+)$ are same:

$$B(Br^-) = B(Bu_4NBBr) - B(Bu_4N^+) = 1.07 - 0.84 = 0.23 \text{ mol}^{-1}$$

$$B(Br^-) = B(NaBr) - B(Na^+) = 0.94 - 0.71 = 0.23 \text{ mol}^{-1}$$

Similarly, the ionic $B$ coefficients for K⁺ ion obtained from different salts has been found to differ only by 0.04 mol⁻¹ and the value reported in Table 2 is the mean of the two values (0.66 ± 0.021 mol⁻¹).

An inspection of Table 2 reveals that the viscosity $B$ coefficient for the cations follows the order: Li⁺ > Na⁺ > K⁺.

The order of decreasing viscosity $B$-coefficients is opposite to the order of decreasing ionic radii of the ions. This suggests that smaller alkali metal ions are more solvated through ion-dipole forces, and solvation of ion decreases with increase in ionic radii. On the other hand, the $B$ coefficients for anions in ethanolamine follow the order: BP₄⁻ > ClO₄⁻ > Br⁻ > I⁻ > NO₃⁻.

This order does not parallel the order of the sizes of the ions (Table 3). However, it is in agreement with the solvation behaviour as indicated by conductance studies\(^7\) of some of these ions in ethanolamine.

The ionic $B_\pm$ coefficients can be used to throw some light on the solvation of ions. This can be done by combining\(^1\) the Einstein equation with that of Jones-Dole equation in the form of Eq. 6,

$$B_\pm = 2.5 \times 4/3\pi R_\pm^3 N_0/1000$$

where $N_0$ is the Avogadro's number. This equation assumes that the solvated ion behaves as a rigid sphere and 2.5 is the shape factor for the sphere. Using the ionic $B$-coefficients, the solvated ionic radii, $R_\pm$ of different ions were calculated with the help of Eq. (6). The calculated solvated ionic radii, $R_\pm$ along...
with the crystallographic radii \((r_c)\) for various ions are recorded in Table 3. It is clear from Table 3 that the \(R_+\) values thus obtained are higher for all the ions as compared with the crystallographic radii, indicating that the ions are solvated in ethanolamine.

The degree of solvation can also be calculated\(^{14}\) in terms of solvation numbers \((n)\) from Eq. 7,
\[
B_\pm = \frac{2.5}{1000}(V_i + nV_s)
\]
where \(V_i\) is the molar volume of the bare ion, and for an ion of radius \(r_i\), its value is \(4/3\pi N_0 r_i^3\) and \(V_s\) is the molar volume of the solvent. Using the molar volume of ethanolamine (60.3 at 25°C), the values of \(n\) were calculated from Eq. (7) and these are given in Table 3.

It is clear from Table 3 that the solvation numbers of cations and anions follow the orders: \(\text{Bu}_4\text{N}^+ < \text{K}^+ < \text{Na}^+ < \text{Li}^+\) and \(\text{NO}_3^- < \text{I}^- < \text{Br}^- < \text{ClO}_4^- < \text{BPh}_4^-\). Though the solvation of cations is understood in terms of their radii, it is difficult to account for the solvation of anions in ethanolamine. Moreover, the value of \(n\) for large \(\text{BPh}_4^-\) is unexpectedly large. Similar unaccountable results have also been noticed\(^{4,15,16}\) in other solvents. This suggests that the behaviour of electrolyte solutions is probably different from the model which gives Eqs (6) and (7). However, in view of the lack of conductometric data, the solvated radii and solvation numbers provide a good comparative study of ions in ethanolamine.

Acknowledgement

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References
10 Falkenhagen J & Vernan E L, Phys Z, 33 (1932) 140.