Solute-solvent interactions of some tetra-alkylammonium salts in 2-methoxyethanol

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The apparent molal volumes ($\phi_\infty$) of six tetra-alkylammonium bromides, namely $\text{Et}_4\text{NBr}$ to $\text{Hep}_4\text{NBr}$, have been determined in 2-methoxyethanol (ME) at 308.15 and 318.15 K. The values have been extrapolated to zero concentration to obtain the limiting values at infinite dilution. Ionic limiting partial molal volumes have also been calculated using the extrapolation method. The results are discussed in terms of ion-ion and ion-solvent interactions.

The present communication reports the study of the apparent molal volumes of some tetra-alkylammonium bromides in 2-methoxyethanol at 308.15 and 318.15 K. This investigation has been undertaken because the temperature dependence of the apparent molal volumes is well known to give more insight regarding ion-ion and ion-solvent interactions which cannot be obtained from apparent molal volume measurements at any given temperature.

Experimental procedure—2-Methoxyethanol (G R E Merck) was distilled twice in an all-glass distillation set before use and the middle fraction collected. The purified solvent had a density of 960.02 kg m$^{-3}$, and a coefficient of viscosity of 1.5414 mPa s at 298.15 K (ref. 10). The densities of pure solvent at 308.15 and 318.15 K are found to be 953.56 and 947.15 kg m$^{-3}$, respectively.

Tetra-alkylammonium bromides (Fluka) were purified by recrystallization and dried under vacuum at elevated temperatures for 12 h.

A stock solution for each salt was prepared by weight and working solutions were obtained by weight dilution. The conversion of the molality into molarity was done by using the density values. The densities were measured according to the procedure reported earlier.

Results and discussion—The apparent molal volumes ($\phi_\infty$) were calculated from the densities of the solutions using Eq. (1)

$$\phi_\infty = M/\rho_0 - 1000(\rho - \rho_0)/C\rho_0$$

where $C$ is the molarity of the electrolyte solution, $M$ is the molecular weight of the solute and $\rho$ and $\rho_0$ are the densities of the solution and solvent, respectively.

The limiting apparent molal volumes, $\phi_\infty^0$, (equal to the partial molal volumes at infinite dilution, $\bar{V}_2^0$) were obtained by least-squares fitting of $\phi_\infty$ values to the Masson equation:

$$\phi_\infty = \phi_\infty^0 + S^*_\phi \sqrt{C}$$

where $S^*_\phi$ is the experimental slope. The plots of $\phi_\infty$ against $\sqrt{C}$ were found to be linear in all cases (Figs 1 and 2), and from the intercept and slope one can obtain the values of $\phi_\infty^0$ and $S^*_\phi$, respectively. The limiting apparent molal volume ($\phi_\infty^0$) and the experimental slope ($S^*_\phi$) are given in Table 1.

![Fig. 1 - Apparent molal volumes $\phi_\infty$ as a function of $\sqrt{C}$ at 308.15 K for (●) $\text{Et}_4\text{NBr}$, (□) $\text{Pr}_4\text{NBr}$, (▲) $\text{Bu}_4\text{NBr}$, (○) $\text{Pen}_4\text{NBr}$, (■) $\text{Hex}_4\text{NBr}$ and (△) $\text{Hep}_4\text{NBr}$](image)
As can be seen from Figs 1 and 2 and also from Table 1 that the $S^*_e$ values for all the salts are positive, thereby, suggesting that the ion-ion interactions are strong in this solvent medium. The positive slopes observed is in accordance with the usual behaviour for solvents having low dielectric constants. The dielectric constant of 2-methoxyethanol is 16.93 at 298.15 K.

The limiting apparent molal volumes ($\phi^0$) are large and positive, and the values increase with increasing size of the cations. This is in agreement with earlier findings in several nonaqueous solvents as well as in water and heavy water\(^4\). The large $\phi^0$ values reveal that the solute-solvent interactions are strong in this medium.

The ionic limiting partial molal volumes have also been calculated\(^13\). The $\bar{V}^0_{\text{ion}}$ values of the tetraalkylammonium bromides in 2-methoxyethanol at 308.15 and 318.15 K were plotted against the formula weight of the corresponding tetraalkylammonium ions. An excellent linear relationship was observed for all the salts. The ionic limiting partial molal volumes ($\bar{V}^0_{\text{ion}}$) are presented in Table 1. The $\bar{V}^0_{\text{ion}}$ values for the tetra-alkylammonium ions are positive and have been found to increase regularly from $\text{Et}_4\text{N}^+$ to $\text{Hep}_4\text{N}^+$. The $\bar{V}^0_{\text{ion}}$ values in 2-methoxyethanol are all found to be almost similar to those in other nonaqueous solvents, e.g., methanol ethylene carbonate, propylene carbonate, formamide, $N,N$-dimethylformamide and $N$-methylacetamide\(^4\). This indicates that the large tetra-alkylammonium ions are scarcely solvated in this solvent medium. The same conclusion has also been reached from conductimetric and viscometric studies\(^14\). The positive $\bar{V}^0_{\text{ion}}$ values indicate that the solvent molecules form a less compact structure around the incorporated ion, thus, giving rise to a positive change in volume. This fact provides additional support in favour of the unsolvation of these ions.

The temperature dependence of $\phi^0$ values can be interpreted in terms of ionic solvation. On raising the temperature, some solvent molecules may be released from the loose solvation layers of the solutes. This is reflected in the greater $\phi^0$ values at higher temperature. The removal of solvent molecules causes increased ion pairing as manifested by the higher $S^*_e$ values with increasing temperature.

### Table 1 — Limiting apparent molal volumes ($\phi^0$) and experimental slopes ($S^*_e$) of tetra-alkylammonium bromides and ionic limiting partial molal volumes ($\bar{V}^0_{\text{ion}}$) in 2-methoxyethanol at 308.15 and 318.15 K

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\phi^0$ cm$^3$mol$^{-1}$</th>
<th>$S^*_e$ cm$^3$L$^{1/2}$mol$^{-3/2}$</th>
<th>$\bar{V}^0_{\text{ion}}$ cm$^3$mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>308.15 K</td>
<td>318.15 K</td>
<td></td>
</tr>
<tr>
<td>Et$_4$NBr</td>
<td>153.22</td>
<td>156.04</td>
<td>13.06</td>
</tr>
<tr>
<td>Pr$_4$NBr</td>
<td>221.51</td>
<td>225.09</td>
<td>5.51</td>
</tr>
<tr>
<td>Bu$_4$NBr</td>
<td>290.94</td>
<td>293.83</td>
<td>7.81</td>
</tr>
<tr>
<td>Pen$_4$NBr</td>
<td>358.05</td>
<td>361.08</td>
<td>7.34</td>
</tr>
<tr>
<td>Hex$_4$NBr</td>
<td>427.01</td>
<td>429.52</td>
<td>6.48</td>
</tr>
<tr>
<td>Hep$_4$NBr</td>
<td>494.60</td>
<td>499.96</td>
<td>6.80</td>
</tr>
</tbody>
</table>

As can be seen from Figs 1 and 2 and also from Table 1 that the $S^*_e$ values for all the salts are positive, thereby, suggesting that the ion-ion interactions are strong in this solvent medium. The positive slopes observed is in accordance with the usual behaviour for solvents having low dielectric constants. The dielectric constant of 2-methoxyethanol is 16.93 at 298.15 K.
References
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