1. Introduction

Ion-solvent interactions have been extensively investigated [1–6] in a number of mixed solvents using different techniques. Alkali ions interact with solvent molecules purely through electrostatic forces [7, 8]. Cu$^+$ and Ag$^+$ ions interact with nitrile solvents also through a special type of interactions [9–11]. Limiting ionic apparent molal isentropic compressibilities ($K_{\alpha, s}^o$) $\pm$ [12–14] are important parameters which not only provide the magnitude but also predict the nature of the interactions on the basis of their positive or negative sign. Even hydrophobic interactions, taking place between tetraalkylammonium ions and solvent molecules, can be identified by evaluation of their ($K_{\alpha, s}^o$) $\pm$ values. In the present work, ion-solvent interactions have been measured in some copper(I), sodium and tetraalkylammonium salts by their isentropic compressibilities. AN and n-BTN mixtures are selected for these studies, because these solvents have different dielectric constants ($\varepsilon_{AN} = 36.0$, $\varepsilon_{n-BTN} = 24.8$) but similar $\equiv C = N$ groups, and are expected to interact with the ions through a different extent of electrostatic but similar special interactions.

2. Experimental

AN 99.5% and n-BTN 99.5% (both E. Merck) were purified as reported in [15]. The purified solvents had the densities 0.77685 and 0.78662 g cm$^{-3}$, viscosities 0.341 and 0.551 cP, and ultrasonic velocities 1280.8 and 1279.0 m s$^{-1}$, respectively, which agree well with the literature values [15].

Copper(I) perchlorate tetraacetonitrile ([Cu(CH$_3$-CN)$_4$]ClO$_4$) was prepared by the reduction of copper(II) perchlorate hexahydrate by copper powder in warm AN, following the method reported by Hathaway et al. [16] and Gill et al. [17]. The purity
of the complex was checked by its elemental and chemical analysis. Tetrabutylammonium tetrphenylborate (Bu$_4$NBPh$_4$) and tetrabutylammonium perchlorate (Bu$_4$NClO$_4$) (used as reference electrolytes in the present work), anhydrous sodium perchlorate (NaClO$_4$) and tetraethylammonium tetraphenylborate (Et$_4$NBPh$_4$) were prepared by the methods given in [18]. NaBPh$_4$, 99.5% (E. Merck), Bu$_4$NI, Bu$_4$NBr, Pr$_4$NBr and Et$_4$NI (all > 99%, from Fluka) were used as received.

Ultrasonic velocity measurements of the binary mixtures as well as of all salt solutions were carried out at 2 MHz frequency with an ultrasonic time intervalometer (Model UTI-101), manufactured by Innovative Instruments (Hyderabad), using a pulse echo over-

valometer (Model UTI-101), manufactured by Innova-

out at 2 MHz frequency with an ultrasonic time inter-

val of 0.2 mol kg$^{-1}$. The limiting apparent molal isentropic compressibility ($K_s$) of each electrolyte in each solvent has been calculated by using the relation

$$K_s = \frac{\eta_o}{\phi_o}$$

(1)

The apparent molal isentropic compressibility ($K_{s,\phi}$) of these salts has been calculated using the partial molal volume $V_\phi$ and the equations

$$V_\phi = \frac{M}{\rho} - \frac{10^3(\rho - \rho_o)}{mp\rho_o},$$

(2)

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
mol\% AN & $\eta_o / \mu Pa$ & $\rho_o / g \cdot cm^{-3}$ & $\phi_o$ & $u_o / ms^{-1}$ & $10^6 K_s^o / bar^{-1}$ \\
\hline
0 & 0.553 & 0.78662 & 24.8 & 1279.0 & 77.71 \\
10 & 0.497 & 0.78379 & 25.7 & 1278.3 & 78.31 \\
20 & 0.405 & 0.78054 & 33.9 & 1276.6 & 78.61 \\
30 & 0.392 & 0.77944 & 37.8 & 1276.3 & 78.91 \\
40 & 0.348 & 0.77685 & 39.7 & 1276.0 & 78.91 \\
50 & 0.310 & 0.77337 & 41.6 & 1275.7 & 78.91 \\
60 & 0.282 & 0.77096 & 43.4 & 1275.4 & 78.91 \\
70 & 0.254 & 0.76862 & 45.2 & 1275.1 & 78.91 \\
80 & 0.226 & 0.76637 & 47.0 & 1274.8 & 78.91 \\
90 & 0.202 & 0.76417 & 48.8 & 1274.5 & 78.91 \\
90 & 0.178 & 0.76197 & 50.6 & 1274.2 & 78.91 \\
90 & 0.154 & 0.75977 & 52.4 & 1273.9 & 78.91 \\
90 & 0.130 & 0.75757 & 54.2 & 1273.6 & 78.91 \\
90 & 0.106 & 0.75537 & 56.0 & 1273.3 & 78.91 \\
90 & 0.082 & 0.75317 & 57.8 & 1273.0 & 78.91 \\
90 & 0.058 & 0.75097 & 59.6 & 1272.7 & 78.91 \\
90 & 0.034 & 0.74877 & 61.4 & 1272.4 & 78.91 \\
90 & 0.010 & 0.74657 & 63.2 & 1272.1 & 78.91 \\
\hline
\end{tabular}
\caption{Viscosity ($\eta_o$), density ($\rho_o$), permittivity ($\varepsilon_o$), ultrasonic velocity ($u_o$) and isentropic compressibility ($K_s^o$) for AN + n-BTN mixtures at 298.15 K.}
\end{table}

3. Results and Discussion

The Physical parameters of the AN + n-BTN bi-

nary mixtures of varying compositions are reported in Table 1, which shows that density ($\rho_o$), viscosity ($\eta_o$) and ultrasonic velocity ($u_o$) of all binary mix-

tures vary over a wide range. The ultrasonic velocities ($u$) and densities ($\rho$) of Bu$_4$NBPh$_4$, Bu$_4$NClO$_4$, Bu$_4$NI, Bu$_4$NBr, Pr$_4$NBr, Et$_4$NI, Et$_4$NBPh$_4$, NaBPh$_4$, NaClO$_4$ and CuClO$_4$ have been measured at different salt molalities ($m$) in the molality range 0.0045 to 2 mol kg$^{-1}$ in AN + n-BTN mixtures containing 0, 20, 40, 60, 80 and 100 mol% AN. The isentropic compressibility ($K_s$) of each electrolyte in each solvent was determined using the equation

$$K_s = \frac{1}{\mu^2\rho}.$$ (3)

where $m$ is the molality and $M$ the molecular mass of the solute. $K_s$ and $K_o$ are the isentropic compressibilities of the solution and the pure solvent, and $\rho$ and $\rho_o$ are the corresponding densities. The plots of $K_{s,\phi}$ versus $m^{1/2}$ were linear in the concentration range studied. The limiting apparent molal isentropic compressibilities ($K_{s,\phi}^o$) were obtained by extrapolation from the linear plots of $K_{s,\phi}$ versus $m^{1/2}$ by the least squares method using the equation

$$K_{s,\phi} = K_{s,\phi}^o + A_{s,\phi} m^{1/2}.$$ (4)

The $K_{s,\phi}^o$ values of the various salts thus obtained are reported in Table 2.

The $K_{s,\phi}^o$ values of these electrolytes are not available for AN + n-BTN mixtures. Therefore a comparison of our values could not be made. In pure AN, the $K_{s,\phi}^o$ values for Bu$_4$NBPh$_4$ (106.5 × 10$^{-4}$ cm$^3$ mol$^{-1}$ bar$^{-1}$) and for Bu$_4$NClO$_4$ (22.6 × 10$^{-4}$ cm$^3$ mol$^{-1}$ bar$^{-1}$) agree within ±2.6 × 10$^{-4}$ cm$^3$ mol$^{-1}$ bar$^{-1}$ with the values 108.0 × 10$^{-4}$ cm$^3$ mol$^{-1}$ bar$^{-1}$ and 20.0 × 10$^{-4}$ cm$^3$ mol$^{-1}$ bar$^{-1}$, respectively [19].

Table 2 shows that the $K_{s,\phi}^o$ values for copper(II) perchlorate and sodium perchlorate are negative and large in AN + n-BTN mixtures at all compositions of the solvent mixtures. For Bu$_4$NBPh$_4$, Bu$_4$NClO$_4$, Bu$_4$NI, Bu$_4$NBr, Pr$_4$NBr, Et$_4$NBPh$_4$ except for NaBPh$_4$, $K_{s,\phi}^o$ is mostly positive and large at all compositions. Et$_4$NI has a negative $K_{s,\phi}^o$ value in AN + n-BTN mixtures, which decreases with increase in mol% of n-BTN.

For obtaining quantitative information regarding the tendency of each ion to produce structural or solvation effects, the $K_{s,\phi}^o$ values for the salts in Table 2 have been split into contributions of individual ions, i. e. into ionic $K_{s,\phi}^o$ values.

As reported in [20–23], the $K_{s,\phi}^o$ values are additive and can be split by that way. For that splitting of
while positive values are obtained mostly for tetra-

stronger ion-solvent interactions involving electro-

components using Ph₄AsBPh₄ as a reference elec-

In Table 3 are written in parentheses in Table 2. Good agreement (within ±2.5 × 10⁻⁴ cm³ mol⁻¹ bar⁻¹) has been observed between the experimental and added up values. Negative \((K_{o,\phi})\) values are generally obtained due to stronger ion-solvent interactions involving electrostatic ion-dipoles, or some special type of interactions, while positive values are obtained mostly for tetra-

alkylammonium ions due to hydrophobic or disper-

sive interactions. The results of Table 3 show that the \((K_{o,\phi})\) values for Cu⁺, Na⁺ and Br⁻ are negative. For Cu⁺ and Na⁺ their magnitude is quite large, but for Br⁻ it is relatively small. The results indicate that Cu⁺ and Na⁺ ions have strong ion-solvent interactions as compared to Br⁻ in all these mixtures. For Cu⁺ and Na⁺ the extent of ion-solvent interactions increases with increase of the n-BTN composition, while for Br⁻ it decreases. The \((K_{o,\phi})\) values for Bu₄N⁺ and Ph₄B⁻ are positive and large at all compositions of the mixtures. These \((K_{o,\phi})\) values indicate some special type of ion-solvent interaction, which may take place due to hydrophobic dispersion or solvent-solvent in-

Table 2. Limiting apparent molal isentropic compressibilities \((K_{o,\phi})\) for some salts in AN + n-BTN mixtures at 298.15 K.

<table>
<thead>
<tr>
<th>Salt</th>
<th>((K_{o,\phi}) / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₄NBPh₄</td>
<td>106.5</td>
</tr>
<tr>
<td>Bu₄NCIO₄</td>
<td>22.6</td>
</tr>
<tr>
<td>Bu₄NI</td>
<td>12.0</td>
</tr>
<tr>
<td>Bu₄NBBr</td>
<td>9.4</td>
</tr>
<tr>
<td>Ph₄NBBr</td>
<td>-4.4</td>
</tr>
<tr>
<td>Et₄NI</td>
<td>-103.8</td>
</tr>
<tr>
<td>Et₄NBPh₄</td>
<td>(-103.5)</td>
</tr>
<tr>
<td>NaBPh₄</td>
<td>-92.2</td>
</tr>
<tr>
<td>NaClO₄</td>
<td>-176.2</td>
</tr>
<tr>
<td>CuClO₄</td>
<td>-212.0</td>
</tr>
</tbody>
</table>

Table 3. Limiting ionic apparent molal isentropic compressibilities \((K_{o,\phi})\) for some ions in AN + n-BTN mixtures at 298.15 K.

<table>
<thead>
<tr>
<th>Ion</th>
<th>((K_{o,\phi}) / 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1})</th>
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<tr>
<td>Bu₄N⁺</td>
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<tr>
<td>Ph₄N⁺</td>
<td>-6.0</td>
</tr>
<tr>
<td>Et₄N⁺</td>
<td>-67.7</td>
</tr>
<tr>
<td>Cu⁺</td>
<td>-186.8</td>
</tr>
<tr>
<td>Na⁺</td>
<td>-151.0</td>
</tr>
<tr>
<td>Ph₄B⁻</td>
<td>58.7</td>
</tr>
<tr>
<td>ClO₄⁻</td>
<td>-25.2</td>
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Using (5) and (6), the \((K_{o,\phi})\) values of Bu₄NBPh₄ were split into contribution of Bu₄N⁺ and Ph₄B⁻ ions. By using these \((K_{o,\phi})\) values, such values for all other ions have been calculated and are reported in Table 3.

The consistency of the present results can be checked by comparing the experimental \((K_{o,\phi})\) values for Et₄NI and NaBPh₄ from Table 2 with the \((K_{o,\phi})\) values obtained by adding up the \((K_{o,\phi})\) values for the respective ions constituting the salts. The added up values for Et₄NI and NaBPh₄ from Table 3 are written in parentheses in Table 2. Good agreement (within ±2.5 × 10⁻⁴ cm³ mol⁻¹ bar⁻¹) has been observed between the experimental and added up values.

Negative \((K_{o,\phi})\) values are generally obtained due to stronger ion-solvent interactions involving electrostatic ion-dipoles, or some special type of interactions, while positive values are obtained mostly for tetra-

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tion for these ions changes from weak electrostatic to a special type of interaction in the n-BTN rich region. As special interaction of Ph$_4$As$^+$ and Ph$_4$B$^-$ with AN through dispersion forces was also reported by Bose and Kundu [24].

For Et$_4$N$^+$ at all compositions and for Pr$_4$N$^+$ only in AN the $(K_{s,\phi}^o)_{\pm}$ values are negative, indicating the solvation of these two ions in these systems. The extent of ion-solvent interactions, however, decreases with the increase of the n-BTN concentration in the mixture.

The $(K_{s,\phi}^o)_{\pm}$ values for Cu$^+$ in some mixed solvents were recently reported in [4]. These results have been incorporated for comparing their ion-solvent interactions with the present system. Plots of $(K_{s,\phi}^o)_{\pm}$ for Cu$^+$ in some solvents mixtures as a function of the mol% AN and TEP are presented in Figs. 1 and 2, respectively. The results show that $(K_{s,\phi}^o)_{\pm}$ for Cu$^+$ becomes most negative between 20 – 60 mol% AN in AN + DMF mixtures, passes through a minimum negative value at about 80 mol% AN in AN + DMSO mixture and changes linearly in AN + n-BTN, AN + TEP, BN + TEP and PY + TEP mixtures with the value becoming more negative and larger with the increase of TEP, NM and n-BTN composition. The ion-solvent behaviour of Cu$^+$ in AN + n-BTN mixtures is similar to that in AN + NM, AN + TEP, BN + TEP and PY + TEP mixtures, but different from that observed in AN + DMF and AN + DMSO mixtures.

4. Conclusions

Cu$^+$, Na$^+$, R$_4$N$^+$ and Ph$_4$B$^-$ ions show strong ion-solvent interactions in AN + n-BTN mixtures. In the cases of Na$^+$ and Cu$^+$ this interaction seems to be mainly due to electrostatic ion-dipole interaction. The interaction between R$_4$N$^+$ and Ph$_4$B$^-$ ions with the solvent molecules appears to be mainly due to hydrophobic or dispersion forces. All anions interact weakly with the solvent molecules in AN + n-BTN mixtures.

Acknowledgement

AK thanks the CSIR, New Delhi for the award of a JRF.