Acoustic characteristics of sodium salt of N-chloro-p-toluene sulphonamide in aqueous and binary aqueous media at 303 K

J Ishwara Bhat* & N V Sabitha+
Department of Chemistry, Manglore University,
Mangalagangothri 574 199, India
*Department of Chemistry, S N College, Kannur 670007, India
Received 28 June 2002; revised 18 September 2002

Acoustic investigation of the sodium salt of N-chloro-p-toluene sulphonamide in water + propan-2-ol, water +propan-1-ol and water +dioxan (upto 80% v/v) has been carried out at 303 K. Various parameters such as adiabatic compressibility, intermolecular free length, specific acoustic impedance, relative association, apparent molar adiabatic compressibility, and solvation number have been computed. Ultrasonic velocity has increased with increase in concentration of N-chloro-p-toluene sulphonamide for a given composition. Adiabatic compressibility and inter molecular free length increase from one composition to another. All these observations have been made use of in establishing the nature of ion-solvent interaction present under existing conditions.

Ultrasonic study is an important aid among the various other available tools for understanding the nature of interaction existing between the different components of a solution. In recent years acoustic studies of electrolytic and non-electrolytic components in many aqueous and non-aqueous media have provided new insights in understanding the nature of ion-solvation.

The sodium salt of N-chloro-p-toluene sulphonamide, chloramine-T or CAT is a stable and inexpensive electrolyte. It has been exploited as an analytical reagent, as an oxidant in kinetic studies and as an electrolyte in solvation studies by several groups. Even though much work has been done on CAT and reported in literature very little work is available as regards to its ultrasonic studies. Hence, herein, we report our results on the ultrasonic studies of CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 K.

Experimental
Chloramine-T (E-Merck) was used as such without further purification. Doubly distilled water and purified organic solvents such as, propan-2-ol, propan-1-ol and dioxan were used to prepare the various mixtures of solvents.

Ultrasonic velocities of solutions of CAT in the composition range 20-80% of co-solvents in water were measured. The concentration range varied from 0.01 to 0.5 mol dm⁻³ for 20-60% composition (v/v) range and from 0.01 to 0.25 mol dm⁻³ in 80% (v/v) of propanols and from 0.01 to 0.2 mol dm⁻³ in 80% (v/v) of dioxan. Solutions of higher concentrations could not be prepared in 80% (v/v) of all the three co-solvents due to the poor solubility of CAT in them. CAT was insoluble in 100% non-aqueous solvents also. Studies were carried out using an ultrasonic interferometer (M-81, Mittal Enterprises, New Delhi) at 2MHz with a measuring frequency tolerance ± 0.03%.

Temperature of the cell was maintained at 303 ± 0.01 K by circulating water in the outer jacket of the cell from a thermostat maintained at the same temperature. The densities of all the solutions were determined by a pyknometer of 15cc capacity. This data coupled with the ultrasonic velocity data were used to calculate various acoustic parameters like adiabatic compressibility ($\beta_{ad}$), intermolecular free length ($L_d$), acoustic impedance ($Z$), relative association ($R_A$), the apparent molar compressibility ($\phi_a$) and the solvation number ($S_a$). On the basis of the above data, the ion-solvent and solvent-solvent interactions existing in the system have been interpreted and an attempt has been made to compare the variation of conductance of CAT in these solvents.

Results and discussion
The adiabatic compressibility ($\beta_{ad}$), intermolecular fee length ($L_d$), specific acoustic impedance ($Z$), relative association ($R_A$), apparent molar adiabatic compressibility ($\phi_a$) and solvation number ($S_a$) have been calculated at 303K using ultrasonic velocity ($\nu$) and density ($d$) values of the solutions. Equations (1-6) have been used to obtain these acoustic parameters.

\[ \beta_{ad} = 1/\nu^2d \]  
\[ L_d = k\sqrt{\beta_{ad}} \]  
\[ Z = ud \]  
\[ R_A = (d_1/d_0)(u_0/\nu)^{1/3} \]  
\[ \phi_a = 1000 (d_0 \beta_{ad} - d_1 \beta_{ad})/d_1 + M_1 \beta_{ad}/d_1 \]
Table 1—Experimentally determined values of ultrasonic velocity at different concentrations of CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 ± 0.01 K

<table>
<thead>
<tr>
<th>C (mol/dm³)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80% (v/v) co-solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + propan-2-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.552</td>
<td>1.632</td>
<td>1.546</td>
<td>1.418</td>
<td>—</td>
</tr>
<tr>
<td>0.40</td>
<td>1.552</td>
<td>1.628</td>
<td>1.544</td>
<td>1.418</td>
<td>—</td>
</tr>
<tr>
<td>0.30</td>
<td>1.550</td>
<td>1.626</td>
<td>1.542</td>
<td>1.416</td>
<td>—</td>
</tr>
<tr>
<td>0.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.286</td>
</tr>
<tr>
<td>0.20</td>
<td>1.534</td>
<td>1.626</td>
<td>1.524</td>
<td>1.416</td>
<td>—</td>
</tr>
<tr>
<td>0.10</td>
<td>1.526</td>
<td>1.608</td>
<td>1.528</td>
<td>1.410</td>
<td>—</td>
</tr>
<tr>
<td>0.05</td>
<td>1.512</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.282</td>
</tr>
<tr>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.282</td>
</tr>
<tr>
<td>0.00</td>
<td>1.508</td>
<td>1.608</td>
<td>1.528</td>
<td>1.410</td>
<td>1.282</td>
</tr>
<tr>
<td>Water + propan-1-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.552</td>
<td>1.610</td>
<td>1.508</td>
<td>1.410</td>
<td>—</td>
</tr>
<tr>
<td>0.40</td>
<td>1.552</td>
<td>1.596</td>
<td>1.506</td>
<td>1.406</td>
<td>—</td>
</tr>
<tr>
<td>0.30</td>
<td>1.550</td>
<td>1.594</td>
<td>—</td>
<td>1.398</td>
<td>—</td>
</tr>
<tr>
<td>0.25</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.314</td>
</tr>
<tr>
<td>0.20</td>
<td>1.534</td>
<td>1.594</td>
<td>—</td>
<td>1.396</td>
<td>—</td>
</tr>
<tr>
<td>0.10</td>
<td>1.526</td>
<td>1.594</td>
<td>1.502</td>
<td>1.391</td>
<td>1.312</td>
</tr>
<tr>
<td>0.05</td>
<td>1.512</td>
<td>1.502</td>
<td>1.502</td>
<td>1.391</td>
<td>1.312</td>
</tr>
<tr>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.312</td>
</tr>
<tr>
<td>0.00</td>
<td>1.508</td>
<td>1.500</td>
<td>1.500</td>
<td>1.396</td>
<td>1.312</td>
</tr>
<tr>
<td>Water + dioxan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.552</td>
<td>1.592</td>
<td>1.604</td>
<td>1.548</td>
<td>—</td>
</tr>
<tr>
<td>0.40</td>
<td>1.552</td>
<td>1.592</td>
<td>1.596</td>
<td>1.548</td>
<td>—</td>
</tr>
<tr>
<td>0.30</td>
<td>1.550</td>
<td>1.590</td>
<td>1.596</td>
<td>1.544</td>
<td>—</td>
</tr>
<tr>
<td>0.20</td>
<td>1.534</td>
<td>1.584</td>
<td>1.586</td>
<td>1.516</td>
<td>1.452</td>
</tr>
<tr>
<td>0.10</td>
<td>1.526</td>
<td>1.584</td>
<td>1.584</td>
<td>1.508</td>
<td>1.448</td>
</tr>
<tr>
<td>0.05</td>
<td>1.512</td>
<td>1.582</td>
<td>1.584</td>
<td>—</td>
<td>1.442</td>
</tr>
<tr>
<td>0.01</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.438</td>
</tr>
<tr>
<td>0.00</td>
<td>1.508</td>
<td>1.580</td>
<td>1.584</td>
<td>1.508</td>
<td>1.438</td>
</tr>
</tbody>
</table>

The adiabatic compressibility $\beta_{ad}$ represents the nature/magnitude of the compressibility of a solvent in the presence of a solute without affecting the enthalpy of the system. It is calculated using Eq(1). From Eq(1) it is clear that $\beta_{ad}$ is the reciprocal of the product of square of ultrasonic velocity and density. Density was determined for all the cases of water + propanols and water + dioxan at 303 ± 0.01 K and is shown in Table 2. Density of the solutions increases...
with increase in concentration for all the compositions of all the three mixtures due to the decrease in volume which is due to electrostriction. Ion-solvent interaction increases with the increase in concentration. The density decreases from one composition to another due to the presence of increased amount of ion-solvent and solvent-solvent interaction in the presence of non-aqueous solvent with water. Solvent mixture is of bigger size compared to pure solvent, which is involved in the solvation. Hence volume increases and density decreases.

For a given composition, since density and ultrasonic velocity increased with increase in concentration, the product \( u' d \) becomes high and the reciprocal \( \beta_{ad} \) decreases with increase in concentration (Table 3). The decrease in \( \beta_{ad} \) may be due to the partial breakdown of the structure of water by dioxan making it less structured. The minima in \( \beta_{ad} \) at 40% dioxan hints at a complex formation in this region. The decrease in compressibility with increase in concentration of CAT is due to the higher electrostriction occurring in the system.

\( \beta_{ad} \) is inversely related to density where as \( L_r \) is directly related to \( \beta_{ad} \) hence \( L_r \) and density becomes inversely related. As density increases \( L_r \) decreases. The experimental observation fully agrees with this idea (Table 4). As \( L_r \) increases, both ion-ion and ion-solvent attractions increase and vice versa. Therefore, as \( L_r \) increases it is expected to have higher ion-solvent interaction leading to smaller electrical conductivity value. The experimental result is in conformity with this fact.

The decrease in ultrasonic velocity with increase in the amount of co-solvent except at 40% (v/v) dioxan brings about a decrease in acoustic impedance \( Z \).
Table 5—Computed values of acoustic impedance at different concentrations of CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 ± 0.01 K

<table>
<thead>
<tr>
<th>c (mol/dm³)</th>
<th>Z×10° (g cm⁻² s⁻¹)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80% (v/v) co-solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water + propan-2-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.613</td>
<td>1.657</td>
<td>1.520</td>
<td>1.337</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>1.596</td>
<td>1.651</td>
<td>1.513</td>
<td>1.336</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>1.581</td>
<td>1.626</td>
<td>1.497</td>
<td>1.322</td>
<td>--</td>
</tr>
<tr>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.117</td>
</tr>
<tr>
<td>0.20</td>
<td>1.555</td>
<td>1.612</td>
<td>1.524</td>
<td>1.362</td>
<td>--</td>
</tr>
<tr>
<td>0.10</td>
<td>1.535</td>
<td>1.574</td>
<td>1.448</td>
<td>1.274</td>
<td>1.098</td>
</tr>
<tr>
<td>0.05</td>
<td>1.512</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.084</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.082</td>
</tr>
<tr>
<td>0.00</td>
<td>1.502</td>
<td>1.597</td>
<td>1.621</td>
<td>1.554</td>
<td>1.481</td>
</tr>
<tr>
<td></td>
<td>Water + propan-1-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.613</td>
<td>1.625</td>
<td>1.481</td>
<td>1.332</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>1.596</td>
<td>1.609</td>
<td>1.415</td>
<td>1.321</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>1.581</td>
<td>1.598</td>
<td>--</td>
<td>1.303</td>
<td>--</td>
</tr>
<tr>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.154</td>
</tr>
<tr>
<td>0.20</td>
<td>1.555</td>
<td>1.580</td>
<td>--</td>
<td>1.285</td>
<td>--</td>
</tr>
<tr>
<td>0.10</td>
<td>1.535</td>
<td>1.564</td>
<td>1.419</td>
<td>1.264</td>
<td>1.131</td>
</tr>
<tr>
<td>0.05</td>
<td>1.512</td>
<td>--</td>
<td>1.411</td>
<td>--</td>
<td>1.126</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.112</td>
</tr>
<tr>
<td>0.00</td>
<td>1.502</td>
<td>1.597</td>
<td>1.621</td>
<td>1.554</td>
<td>1.481</td>
</tr>
<tr>
<td></td>
<td>Water + dioxan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.613</td>
<td>1.675</td>
<td>1.706</td>
<td>1.655</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>1.596</td>
<td>1.667</td>
<td>1.688</td>
<td>1.655</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>1.581</td>
<td>1.648</td>
<td>1.654</td>
<td>1.544</td>
<td>--</td>
</tr>
<tr>
<td>0.20</td>
<td>1.555</td>
<td>1.629</td>
<td>1.649</td>
<td>1.589</td>
<td>1.522</td>
</tr>
<tr>
<td>0.10</td>
<td>1.535</td>
<td>--</td>
<td>1.632</td>
<td>1.565</td>
<td>1.505</td>
</tr>
<tr>
<td>0.05</td>
<td>1.512</td>
<td>1.613</td>
<td>1.627</td>
<td>--</td>
<td>1.493</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>1.605</td>
<td>--</td>
<td>--</td>
<td>1.482</td>
</tr>
<tr>
<td>0.00</td>
<td>1.502</td>
<td>1.597</td>
<td>1.621</td>
<td>1.554</td>
<td>1.481</td>
</tr>
</tbody>
</table>

Table 6—Computed values of relative association at different concentrations of CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 ±0.01 K—Contd

<table>
<thead>
<tr>
<th>c (mol/dm³)</th>
<th>R_A</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80% (v/v) co-solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water + propan-2-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>1.109</td>
<td>1.111</td>
<td>1.111</td>
<td>1.013</td>
<td>--</td>
</tr>
<tr>
<td>0.05</td>
<td>1.104</td>
<td>--</td>
<td>1.007</td>
<td>--</td>
<td>1.033</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.005</td>
</tr>
<tr>
<td></td>
<td>Water + propan-1-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>1.182</td>
<td>1.113</td>
<td>1.163</td>
<td>1.138</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>1.132</td>
<td>1.152</td>
<td>1.155</td>
<td>--</td>
<td>1.137</td>
</tr>
<tr>
<td>0.30</td>
<td>1.123</td>
<td>1.141</td>
<td>1.276</td>
<td>--</td>
<td>1.124</td>
</tr>
<tr>
<td>0.20</td>
<td>1.117</td>
<td>1.133</td>
<td>1.132</td>
<td>--</td>
<td>1.117</td>
</tr>
<tr>
<td>0.10</td>
<td>1.109</td>
<td>1.140</td>
<td>1.007</td>
<td>--</td>
<td>1.095</td>
</tr>
<tr>
<td>0.05</td>
<td>1.104</td>
<td>1.118</td>
<td>1.003</td>
<td>--</td>
<td>1.091</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 7—Calculated values of apparent molar compressibility at different concentrations of CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 ± 0.01 K

<table>
<thead>
<tr>
<th>c (mol/dm³)</th>
<th>φₐ×10⁻¹⁹ (cm² mol⁻¹)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80% (v/v) co-solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water + propan-2-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>66.5</td>
<td>55.1</td>
<td>63.1</td>
<td>71.5</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>78.7</td>
<td>61.4</td>
<td>69.3</td>
<td>81.3</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>88.4</td>
<td>89.7</td>
<td>79.2</td>
<td>--</td>
<td>92.9</td>
</tr>
<tr>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>127.9</td>
</tr>
<tr>
<td>0.20</td>
<td>105.7</td>
<td>93.9</td>
<td>111.1</td>
<td>116.2</td>
<td>--</td>
</tr>
<tr>
<td>0.10</td>
<td>120.0</td>
<td>122.2</td>
<td>136.3</td>
<td>200.5</td>
<td>--</td>
</tr>
<tr>
<td>0.05</td>
<td>133.1</td>
<td>--</td>
<td>--</td>
<td>220.5</td>
<td>--</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>224.6</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Water + propan-1-ol</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>66.5</td>
<td>69.2</td>
<td>75.1</td>
<td>80.2</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>78.7</td>
<td>77.7</td>
<td>80.6</td>
<td>92.7</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>88.4</td>
<td>84.0</td>
<td>--</td>
<td>106.8</td>
<td>--</td>
</tr>
<tr>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>145.3</td>
</tr>
<tr>
<td>0.20</td>
<td>105.7</td>
<td>95.5</td>
<td>--</td>
<td>121.6</td>
<td>--</td>
</tr>
<tr>
<td>0.10</td>
<td>120.0</td>
<td>107.3</td>
<td>128.5</td>
<td>160.4</td>
<td>185.2</td>
</tr>
<tr>
<td>0.05</td>
<td>133.1</td>
<td>--</td>
<td>135.1</td>
<td>--</td>
<td>189.1</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>220.7</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Water + dioxan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>66.5</td>
<td>65.0</td>
<td>60.1</td>
<td>53.8</td>
<td>--</td>
</tr>
<tr>
<td>0.40</td>
<td>78.7</td>
<td>69.5</td>
<td>74.9</td>
<td>61.4</td>
<td>--</td>
</tr>
<tr>
<td>0.30</td>
<td>88.4</td>
<td>80.0</td>
<td>81.7</td>
<td>68.1</td>
<td>--</td>
</tr>
<tr>
<td>0.20</td>
<td>--</td>
<td>94.0</td>
<td>97.3</td>
<td>93.9</td>
<td>103.4</td>
</tr>
<tr>
<td>0.10</td>
<td>105.7</td>
<td>100.5</td>
<td>104.4</td>
<td>109.2</td>
<td>115.2</td>
</tr>
<tr>
<td>0.05</td>
<td>133.1</td>
<td>105.3</td>
<td>104.0</td>
<td>--</td>
<td>124.0</td>
</tr>
<tr>
<td>0.01</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>131.9</td>
<td>--</td>
</tr>
</tbody>
</table>

Accordingly Z decreased with increase in co-solvent in all the three cases except in the case of 40%(v/v) dioxan where it showed an increase (Table 5).

Relative association, R_A, is the association of solvent molecules to the ions because of the breaking
Table 8—Computed values of limiting apparent molar compressibility and slope for CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 ± 0.01 K

<table>
<thead>
<tr>
<th>Solvent</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80% (v/v)</th>
<th>Co-solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>water+propan-2-ol</td>
<td>$\Phi_k \times 10^{10}$</td>
<td>170.0</td>
<td>146.0</td>
<td>170.0</td>
<td>188.0</td>
<td>286.0</td>
</tr>
<tr>
<td></td>
<td>$S_k \times 10^{10}$</td>
<td>-140.0</td>
<td>-133.3</td>
<td>-163.6</td>
<td>-155.5</td>
<td>-342.9</td>
</tr>
<tr>
<td>water+propan-1-ol</td>
<td>$\Phi_k \times 10^{10}$</td>
<td>170.0</td>
<td>140.0</td>
<td>170.0</td>
<td>202.0</td>
<td>238.0</td>
</tr>
<tr>
<td></td>
<td>$S_k \times 10^{10}$</td>
<td>-140.0</td>
<td>-105.2</td>
<td>-153.3</td>
<td>-173.3</td>
<td>-200.0</td>
</tr>
<tr>
<td>water+dioxan</td>
<td>$\Phi_k \times 10^{10}$</td>
<td>170.0</td>
<td>130.0</td>
<td>154.0</td>
<td>158.0</td>
<td>140.0</td>
</tr>
<tr>
<td></td>
<td>$S_k \times 10^{10}$</td>
<td>-140.0</td>
<td>-95.2</td>
<td>-84.2</td>
<td>-84.2</td>
<td>-84.2</td>
</tr>
</tbody>
</table>

Table 9—Computed values of solvation number for different concentrations of CAT in various compositions of water + propan-2-ol/propan-1-ol/dioxan at 303 ± 0.01 K

<table>
<thead>
<tr>
<th>c mol/dm$^3$</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80% (v/v)</th>
<th>co-solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water + propan-2-ol</td>
<td>0.50</td>
<td>10.0</td>
<td>5.0</td>
<td>6.0</td>
<td>4.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>13.0</td>
<td>5.0</td>
<td>4.0</td>
<td>4.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>6.0</td>
<td>5.0</td>
<td>--</td>
<td>--</td>
<td>6.0</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>12.0</td>
<td>--</td>
<td>7.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Water + propan-1-ol</td>
<td>0.05</td>
<td>12.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>8.0</td>
</tr>
<tr>
<td>Water + dioxan</td>
<td>0.50</td>
<td>10.0</td>
<td>5.0</td>
<td>5.0</td>
<td>4.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>13.0</td>
<td>5.0</td>
<td>4.0</td>
<td>4.0</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>12.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

up of dipolar solvent molecules by the ions. The breaking up of the solvent molecule structure to orient themselves about the central ion will be facilitated by its dipolar nature and also due to the polarisability of the central ion. Hence as the number of ions increased in a solution, $R_A$ is expected to increase compared to the pure solvent. $R_A$ increased with increase in concentration for a given composition and decreased with increase in percentage composition for a given concentration in the case of water + propanol mixture as shown in Table 6. But this ideal trend is not fully obeyed by water + dioxan mixture.

The apparent molar compressibility $\Phi_k$ was calculated from the ultrasonic velocity and density values using Eq. (5) and are shown in Table 7. The computed values of limiting apparent molar compressibility and slope for CAT in various compositions of water+propan-2-ol/propan-1-ol/dioxan at 303 ± 0.01 K are given in Table 8.

This also represents the magnitude of ion-solvent interaction. The values of $\Phi_k$ is found to decrease linearly with concentration.

Solvation number $S_n$ is the number of solvent molecules attached to the central ion in the form of a primary solvation shell, which is determined experimentally using Eq. (6). Such resulted data are shown in Table 9. In case of water the solvation number is found to be an abnormal value of 10 compared to the reported value of 6. It is difficult to explain this discrepancy with this available limited data. But in the case of solvent mixture of water + propanols and water + dioxan, the solvation number is found to be around six as expected.

Acknowledgement

NVS is thankful to the UGC, New Delhi for awarding scholarship under the faculty improvement programme.

References