Ultrasonic and viscometric studies of substituted flavone, isoxazole and pyrazole in 70 % acetone-water mixture

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Ultrasonic velocity and viscosity-density of 4′-methoxy-3-(p-methoxy cinnamoyl) flavone (L1), 3-(2-hydroxy-5-methylphenyl)-4-benzoyl-5-(p-methoxyphenyl) isoxazole (L2) and 3-(2-hydroxy-5-methylphenyl)-5-methylpyrazole (L3) at different molalities in 70% (v/v) acetone-water mixture have been measured at 298.5 ± 0.1 K. The values of relative viscosity (ηr), apparent molal volume (φ), and adiabatic compressibility (βad) have been used in the present note. An attempt has been made to determine the densities, viscosities and ultrasonic velocities of 4′-methoxy-3-(p-methoxy cinnamoyl) flavone (L1), 3-(2-hydroxy-5-methylphenyl)-4-benzoyl-5-(p-methoxy phenyl) isoxazole (L2) and 3-(2-hydroxy-5-methylphenyl)-5-methylpyrazole (L3) at different molalities in 70% (v/v) acetone-water mixture at 298.5 ± 0.1 K. The data obtained have been used in the present investigation to study various interactions.

Experimental

The solutes (L1, L2, L3) used in the present investigation were prepared by standard methods. The solvent used was of A R grade and doubly distilled water was used. Densities and viscosities of solutions were measured with the help of bicapillary pyknometer and an Ostwald type viscometer at 298.5 ± 0.1 K. The values were accurate to within ± 0.1 % kg m⁻³ and ± 0.11 % kg m⁻¹s⁻¹ respectively. All the weighings were made on Mechaniki Zaktady Preczyznej Gdansk Balance (± 0.001 gm). The velocity of ultrasonic waves were determined by using variable path, single crystal interferrometer (Mittal enterprises, model MX-3) operating at a frequency of 1 MHz with accuracy of ± 0.03 %.

Results and discussion

Density (d), relative viscosity (ηr), apparent molal volume (φ), ultrasonic velocity (U), adiabatic compressibility (βad), apparent molal compressibility (φκad), intermolecular free length (L0), relative association (RA) and specific acoustic impedance (Z) of the solutions at different concentrations (1.0×10⁻³, 1.5×10⁻³, 2.0×10⁻³, 2.5×10⁻³, 3.0×10⁻³, and 3.5×10⁻³ M) have been measured at 298.5 ± 0.1 K and are presented in Table 1. The values of density and relative viscosity of these systems increase with increase in concentration of the solutes. The increase in viscosity with increase in concentration may be attributed to the increase in solute-solvent interactions. Solutes are surrounded by solvent molecules and the degree of cluster formation is less. They behave as structure breakers. Viscosity data were analysed in the light of Jones-Dole equation.

\[
(\eta_r-1)\sqrt{c} = A + B \sqrt{c}
\]

where A and B are the Falkenhagen and the Jones-Dole coefficients. These coefficients were obtained from the intercepts and slopes of the linear plots of (ηr-1)√c versus √c. The lower value of A coefficient indicates the presence of very weak ion-ion interactions (Table 2). It is evident from Table 2 that the B-coefficient is an adjustable parameter, which may be either positive or negative, and it is a measure of the effective hydrodynamic volume of solutes which accounts for the ion-solvent interactions. It is also known as measure of order or disorder introduced by the ions or solute into the
Table 1—Values of different parameters of L1, L2 and L3 in 70% (v/v) acetone-water mixture from viscosity and ultrasonic study at 298.5±0.1 K

<table>
<thead>
<tr>
<th>Concentration</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>M×10^3 (mol dm⁻³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d (g cm⁻³)</td>
<td>0.8289</td>
<td>0.8348</td>
<td>0.8428</td>
<td>0.8447</td>
<td>0.8483</td>
<td>0.8516</td>
</tr>
<tr>
<td>η (1.4537)</td>
<td>1.5106</td>
<td>1.5318</td>
<td>1.5420</td>
<td>1.5553</td>
<td>1.5682</td>
<td></td>
</tr>
<tr>
<td>U×10² (cm s⁻¹)</td>
<td>1474.06</td>
<td>1405.94</td>
<td>1399.37</td>
<td>1389.93</td>
<td>1387.54</td>
<td>1367.43</td>
</tr>
<tr>
<td>β×10⁴ (bar⁻¹)</td>
<td>55.5223</td>
<td>60.6016</td>
<td>60.5913</td>
<td>61.2790</td>
<td>61.2293</td>
<td>62.7992</td>
</tr>
<tr>
<td>L×10² (A⁰)</td>
<td>4.4847</td>
<td>4.6853</td>
<td>4.6849</td>
<td>4.7114</td>
<td>4.7095</td>
<td>4.7695</td>
</tr>
<tr>
<td>φ×10⁻¹ (cm mol⁻¹)</td>
<td>2.0248</td>
<td>1.2947</td>
<td>1.2947</td>
<td>1.348</td>
<td>1.105</td>
<td>0.9099</td>
</tr>
<tr>
<td>R × 10² (g cm⁻² S⁻¹)</td>
<td>0.8370</td>
<td>0.8563</td>
<td>0.8659</td>
<td>0.8698</td>
<td>0.8740</td>
<td>0.8817</td>
</tr>
</tbody>
</table>

Solutes A B φ₀ φₗ(kₗ)×10² (cm mol⁻¹ bar⁻¹) S
L₁ 21.2 -208.33 5.0013 0.5241 -0.97
L₂ 20.1 -176.47 5.1120 0.7540 -0.91
L₃ 19.6 -156.66 5.4990 0.7601 -0.99

The small values of φ₀ indicate weaker solute-solvent interactions at infinite dilution. Sᵥ is a measure of solute-solute interactions. The negative values of Sᵥ show that the interactions are weak and less complex ion formation takes place.

The values of φₗ(kₗ) are found to be decreasing with increase in the concentration of solute. The positive values of φₗ(kₗ) show the electrostatic force in the vicinity of ions causing solvation of solute.

The inter molecular free length (Lₗ) increases with increase in the concentration of solute and ultrasonic velocity decreases. This indicates that there is a weak
solute-solvent interaction. This may also imply the increase in number of free ions, showing the occurrence of ionic dissociation due to weak ion-ion interactions. The increase of $\beta$ with the concentration may be due to departure of solvent molecules around the ions.

The relative association ($R_A$) is influenced by two factors: (i) The breaking up of the solvent molecules on addition of solute to it; and (ii) the solvation of solutes that are simultaneously present.

The former results in decrease and the latter in increase of $R_A$. The increase of $R_A$ with concentration suggests that solvation of solutes predominates over the breaking up of the solvent molecules. It is observed that there is linear variation of $R_A$ and non-linear variation of $Z$ with concentration.

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References