Original Article

THERMODYNAMIC PROPERTIES OF L-THREONINE IN AQUEOUS SOLUTIONS OF KNO₃ AT 303 K

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Abstract

Density, viscosity and ultrasonic velocity of L-threonine in aqueous potassium nitrate (0.04, 0.06 and 0.08M) solutions have been measured as a function of concentration of amino acid and electrolyte at 303 K. Experimental data have been used to estimate the adiabatic compressibility (β), change in adiabatic compressibility (Δβ), relative change in adiabatic compressibility (Δβ/β₀), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ'_k), limiting apparent molal volume (ϕ'_v) and their constants (S_k, S_v) and viscosity B-coefficient. These parameters have been interpreted in terms of ion- ion and ion-solvent interactions.

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Key words: Ultrasonic velocity, intermolecular/interionic interaction, threonine, KNO₃.

1.1 INTRODUCTION

Salts have large effects on the structure and properties of proteins [1]. The effect of electrolytes on structure and function of both proteins and nucleic acids has been widely studied in terms of their structure making and structure breaking properties. Proteins are complex molecules and their behavior in solutions is governed by a combination of many specific interactions, it is a good approach to study simpler model compounds such as amino acids and peptides which are basic building blocks of the proteins. The standard α-amino acids have special importance among the other chemical groups since they are found in all naturally occurring proteins, which play a vital role in nearly all chemical and biological process [2].

The interaction of amino acid with aqueous solutions of electrolyte plays a very important role in undertaking the nature of action of bioactive molecules and / or the thermodynamic behaviour of biochemical processes in the body system. In fact many studies on the thermodynamic properties of amino acids in aqueous electrolyte solutions have been reported in the past [3-5]. To the best of our knowledge, ultrasonic velocity, density and viscosity study of threonine with aqueous KNO₃ is not reported up to now. Threonine is an essential amino acid, it plays a vital role in human nutrition and promotes normal growth by helping to maintain the proper protein balance in the body.

In the present paper, we report that density, viscosity and ultrasonic velocity of ternary system of L-threonine in aqueous KNO₃ (0.04, 0.06 and 0.08M) were measured at 303K. From these experimental data, a number of thermodynamic parameters namely, adiabatic compressibility (β), change in adiabatic compressibility (Δβ), relative change in adiabatic compressibility (Δβ/β₀), apparent molal compressibility (ϕ_k), apparent molal volume (ϕ_v), limiting apparent molal compressibility (ϕ'_k), limiting apparent molal volume (ϕ'_v) and their constants (S_k, S_v) and viscosity B-coefficient have been calculated. These parameters were utilized to study various interactions taking place in the solutions of L-threonine in aqueous KNO₃.

1.2 EXPERIMENTAL DETAIL

Analytical reagent (AR) grade with minimum assay of 99.9 % of threonine and potassium nitrate were obtained from SD fine Chemicals, was used as such without further purification. Water used in the experiment was deionised and degassed prior to making solutions. Aqueous solutions of KNO₃ (0.04, 0.06 and 0.08M) were prepared and there were used as a solvent to prepare the threonine solutions. All the solutions were prepared in a dry box and stored in a special air tight bottle. The weighing was done on an electronic digital balance with a precision of ± 0.1mg. The density of the solvent and ternary mixture was measured using a specific gravity bottle by relative measurement method with an accuracy of 0.01 kgm⁻³. An Ostwald’s viscometer was
Table 1: Density, viscosity, ultrasonic velocity, adiabatic compressibility, change and relative change in adiabatic compressibility of threonine in binary aqueous solutions of KNO₃ at 303K.

<table>
<thead>
<tr>
<th>Threonine (molar kg⁻¹)</th>
<th>ρ  Kg m⁻³</th>
<th>η  x 10⁴ N s m⁻²</th>
<th>U  ms⁻¹</th>
<th>β  x 10¹⁰ Pa⁻¹</th>
<th>- Δβ  x 10¹² Pa⁻³</th>
<th>- Δβ/β x 10⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 0.04 mol. kg⁻¹ KNO₃</td>
<td>1015.8</td>
<td>0.8060</td>
<td>1506.8</td>
<td>4.3359</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.02 0.06 mol. kg⁻¹ KNO₃</td>
<td>1017.4</td>
<td>0.8167</td>
<td>1510.4</td>
<td>4.3085</td>
<td>2.74</td>
<td>6.33</td>
</tr>
<tr>
<td>0.04 0.08 mol. kg⁻¹ KNO₃</td>
<td>1019.2</td>
<td>0.8280</td>
<td>1514.0</td>
<td>4.2804</td>
<td>5.55</td>
<td>12.79</td>
</tr>
<tr>
<td>0.06 0.10 mol. kg⁻¹ KNO₃</td>
<td>1021.0</td>
<td>0.8386</td>
<td>1517.2</td>
<td>4.2549</td>
<td>8.10</td>
<td>18.69</td>
</tr>
<tr>
<td>0.08 0.12 mol. kg⁻¹ KNO₃</td>
<td>1022.8</td>
<td>0.8496</td>
<td>1520.2</td>
<td>4.2307</td>
<td>10.53</td>
<td>24.28</td>
</tr>
<tr>
<td>0.10 0.14 mol. kg⁻¹ KNO₃</td>
<td>1024.6</td>
<td>0.8605</td>
<td>1523.0</td>
<td>4.2077</td>
<td>12.82</td>
<td>29.57</td>
</tr>
</tbody>
</table>

used for the viscosity measurement. The ultrasonic velocity was measured using a single crystal variable path interferometer at 2 MHz. The temperature of the solution was maintained at 303K in an electronically controlled thermostatic waterbath. The accuracy in the temperature measurement is ± 0.1 K.

RESULTS AND DISCUSSION

The density (ρ), viscosity (η), ultrasonic velocity (u), adiabatic compressibility (β), change in adiabatic compressibility (Δβ) and relative change in adiabatic compressibility (Δβ/β) of threonine in aqueous solutions of KNO₃ (0.04, 0.06 and 0.08 M) at 303 K are given in Table 1. The values of acoustic impedance (Z), apparent molal compressibility (ϕ₀) and apparent molal volume (ϕ₀) for the ternary solutions are presented in Table 2. Limiting apparent molal compressibility (ϕ₀) and limiting apparent molal volume (ϕ₀) and their constants (S₁ and S₂) and viscosity coefficient of A and B parameters of Jone-Dole equations have been computed and reported in Table 3.

Density is known to be a measure of ion-solvent and solvent –solvent interactions. From the Table 1, the density increases with increase in solute concentration as well as KNO₃ content. The increase in density may be interpreted as structure – making nature of the solvent due to the solute.

Viscosity is one of the most important properties of many technological and scientific applications and therefore it has been a subject of an enormous effort of the measurement and interpretation for liquid mixtures [6]. In the present systems, the viscosity increases with increase in the concentration of solute as well as increasing KNO₃ content and this indicates the presence of ion-solvent interaction.

Ultrasonic velocity values increases with increase in concentration of amino acid as well as KNO₃ content. The increasing trend suggests a moderate strong electrolytic nature in the solute (threonine) tend to attract the solvent molecules. Molecular association is thus responsible for the observed increase in ultrasonic velocity in these mixtures. When the amino acid is dissolved in KNO₃ + water mixtures, the cation NH₄⁺ and anion COO⁻ are formed. The K⁺ and NO₃⁻ ions furnished by electrolytes interact electrostatically with NH₄⁺ and anion COO⁻ groups of amino acid zwitterions. In addition, the water dipoles are strongly aligned to the cations/anions as well as the amino acid zwitterions by electrostatic forces. These interactions comprehensively introduce the cohesion into solutions under investigation. The cohesive forces are further enhanced on successive increases in concentration of solute as well as KNO₃ content. The added amount of amino acid zwitterions may also occupy the cavities of water clusters which may lead to the formation of denser structure of the aqueous electrolyte solutions. This process may have continued until a concentration of solute is reached at which all cavities are filled. Riyazuddin and Bansal [7], Shahina Islam and Waris, [8] and Yasmin Akhtar and Ibrahim, [9] have reported similar increasing trend of
Table 2: Acoustic impedance, apparent molal compressibility and apparent molal volume of ternary solutions

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Salt content</th>
<th>Threonine (m(mol.kg⁻¹))</th>
<th>Z × 10⁻⁶ kg m⁻² s⁻¹</th>
<th>-φₚ × 10⁸ m² N⁻¹</th>
<th>-φᵥ × 10³ m³ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-threonine</td>
<td>0.04</td>
<td>1.5306</td>
<td>-</td>
<td>78.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>1.5431</td>
<td>-</td>
<td>83.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>1.5489</td>
<td>-</td>
<td>86.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>1.5605</td>
<td>-</td>
<td>86.63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>1.5449</td>
<td>-</td>
<td>83.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>1.5512</td>
<td>-</td>
<td>83.62</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>1.5570</td>
<td>-</td>
<td>88.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>1.5685</td>
<td>-</td>
<td>88.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>1.5646</td>
<td>-</td>
<td>89.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>1.5702</td>
<td>-</td>
<td>89.45</td>
<td></td>
</tr>
</tbody>
</table>

Table 3: Limiting apparent molal compressibility, limiting apparent molal volume and their constants (Sₖ and Sᵥ) and A and B parameters of Jones – Dole equation for ternary mixtures.

<table>
<thead>
<tr>
<th>Amino acid</th>
<th>Salt content</th>
<th>φ₀ × 10⁸ m² N⁻¹</th>
<th>Sₖ × 10⁸ N⁻¹ m⁻¹ mol⁻¹</th>
<th>φ₀ × 10³ m³ mol⁻¹</th>
<th>Sᵥ m³ Kg⁻¹ mol⁻³²</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-threonine</td>
<td>0.04</td>
<td>-17.574</td>
<td>8.587</td>
<td>-78.610</td>
<td>-91.563</td>
<td>-0.0006</td>
<td>0.6780</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>-17.123</td>
<td>9.280</td>
<td>-82.128</td>
<td>-74.051</td>
<td>-0.0059</td>
<td>0.6786</td>
</tr>
</tbody>
</table>

variation of ultrasonic velocity with increase in solute concentration in amino acid + salt + water, Leucine /NaCl/KCl in aqueous urea and glycine in aqueous MgCl₂/NaCl systems respectively.

Adiabatic compressibility

The adiabatic compressibility of the amino acid in aqueous electrolyte solutions have been calculated from the ultrasonic velocity and density data using the relation

\[ \beta = \frac{1}{U^2 \rho} \]

The observed values of adiabatic compressibility, Table 3 are found to decrease with increase in the concentration of solute as well as KNO₃ content. However, the decrease in \( \beta \) is more marked in 0.08 M electrolyte solution and become less so as the 0.04 M concentration of the electrolyte. This clearly suggested that the strength of interaction in the system increase with increasing concentration of electrolyte in the solutions.

Change and relative change in adiabatic compressibility

The change and relative change in adiabatic compressibility values have been obtained by using the following equations,

\[ \Delta \beta = \beta - \beta_0 \]  
\[ \Delta \beta / \beta_0 \]  
\[ \Delta \beta / \beta_0^0 \]

where \( \beta_0 \) and \( \beta \) are the adiabatic compressibility of solvent and solutions, respectively. The calculated values of \( \Delta \beta \) and \( \Delta \beta / \beta_0 \) show an increasing trend of variation with increase in
concentration of amino acid. This may be attributed to an increase in the incompressible part in a solution. Similar conclusion was reported by Riyazudddeen and Bansal [7].

**Acoustic impedance**

The specific acoustic impedance is the product of density and ultrasonic velocity of solvent / solution and can be expressed as

\[ Z = \rho_0 u_0 \]  

(4)

The values of Z (Table 2) increase with increase in solute concentration. Such behaviour reinforces the view that complex formation does not occur among the components of solution. The trend of variation of Z with solute concentration is similar to those exhibited by the variation of ultrasonic velocity values (Shahina Islam and Waris, [8]).

**Apparent molal compressibility**

The density and adiabatic compressibility values were employed for calculating apparent molal compressibility \( \phi_k \) of solute in aqueous electrolyte solutions at different concentration using the equation

\[ \phi_k = \frac{1000}{m_0} \rho \beta_0 \left( \rho_0 \beta \rho - \beta_0 \rho \right) + \frac{\beta_0 M}{\rho_0} \]  

(5)

The values of \( \phi_k \) are non-linear and negative (Table 2) over the entire range of molality of amino acid and also an increase of potassium nitrate content. The negative values of \( \phi_k \) indicating the electrostrictive and hydrophilic interaction occurring in the system, thereby indicating solute-solvent interaction (Thirumaran and Job Sabu [10]) which is in good agreement with the results reported for some amino acids in binary aqueous solutions of MgCl\(_2\)-6H\(_2\)O (Amalendu Pal and Suresh Kumar [11]). The values of \( \phi_k \) were fitted to the equation

\[ \phi_k = \phi_k^0 + S_k^m \]  

(6)

where \( \phi_k^0 \) and \( S_k \) are the limiting apparent molal compressibility and related constant respectively. \( \phi_k^0 \) provides information regarding solute – solvent interaction and \( S_k \), gives the idea of solute –solvent interaction in the solution. The calculated values of \( \phi_k^0 \) and \( S_k \) are included in Table 3. The values of \( \phi_k^0 \) are negative over the entire range of KNO\(_3\) content. The negative \( \phi_k^0 \) values may be due to loss of compressibility of solvent because of strong electrostrictive forces of ions [12]. The value of \( S_k \) exhibit both positive and negative. This behavior indicates the existence of ion-ion/ solute-solute interactions. It is well known that solutes electrostriction lead to decrease in the compressibility of the solution. This is reflected by negative value of \( \phi_k \) of the systems [13].

**Apparent molal volume**

The apparent molal volumes (\( \phi_v \)) were calculated from measured density data using the following equation

\[ \phi_v = \frac{1000}{m_0} \rho_0 \left( \rho_0 - \rho \right) + \left( \frac{M}{\rho_0} \right) \]  

(7)

where M, molecular weight of the solute, m is the molality of the solutions, \( \rho \) and \( \rho_0 \) are the density of solution and solvent, respectively. The negative values of \( \phi_v \) indicate the solute – solvent and electrostrictive salvation of ions [14].

The limiting apparent molal volume was obtained by least square fitting method of the following equation

\[ \phi_v = \phi_v^0 + S_v^m \]  

\[ \left( \frac{\eta}{\eta_0} - 1 \right) \left( \frac{m}{m_0} \right)^{1/2} = A + Bm^{1/2} \]  

(8)

(9)

where \( \phi_v^0 \) and \( S_v \) are the limiting apparent volume and related constant respectively and are summarized in Table 3. The negative values of \( \phi_v^0 \) indicate the presence of solute-solvent interaction. The values of \( S_v \) are found to be negative in all the systems, suggesting the presence of weak solute-solute interaction.

**Viscosity B-coefficient**

The viscosity data obtained for ternary systems as a function of amino acid and electrolyte concentration are reported in Table 3. The viscosity B-coefficient for the amino acid in aqueous KNO\(_3\) solution were calculated from the following equation,

\[ \frac{\eta}{\eta_0} - 1 = A + Bm^{1/2} \]  

(9)

The values of A are negative and B-coefficient are positive. Since A is a measure of ionic interaction [15], it is evident that there is a weak ion-ion interaction in the amino acid studied, which is indicated by the smaller magnitude of A values. B-coefficient is known as a measure of ion – solvent interaction and is directly dependent on the size, shape and charge of the solute molecules. Thus, B values reflect the net structural effects of the solute and solvent molecules. The positive behaviour of B-coefficient suggests the existence of strong ion-solvent interaction. The large values of B indicate structure making capacities of the solute.

**References**


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