INTERMOLECULAR INTER-IONIC INTERACTIONS OF L-ISOLEUCINE, L-PROLINE AND L-GLUTAMINE WITH K₂SO₄ AT DIFFERENT TEMPERATURES RANGING FROM 303.15 K - 323.15 K

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ABSTRACT

Ultrasonic velocity and density values have been measured for ternary systems (amino acid + salt + water): L-isoleucine, L-proline and L-glutamine in aqueous $0.5M K_2SO_4$ solution used as solvent for several concentrations of amino acids at different temperatures in the range of 303.15 to 323.15K. The ultrasonic velocity values have been found to increase with increase in amino acid concentration and temperature in all the systems. The increase in ultrasound velocity with increase in concentration has been discussed in terms of electrostatic interactions occurring between terminal groups of zwitter-ions (NH⁴⁺ and COO⁻) and K⁺, SO4⁻² ions. The interactions of water dipoles with cations/anions and with zwitter-ions have also been taken into consideration. It has been observed that the ion-zwitter-ion and ion-dipole attractive forces are stronger than those of ion-hydrophobic repulsive forces.

KEYWORDS: Intermolecular/Interionic Interactions, L-isoleucine, L-proline, Lglutamine, K₂SO₄

I. INTRODUCTION

As amino acids and peptides are the building blocks of the proteins, their study provides important information, which can be related to the behaviour of larger biomolecules such as proteins. Thermodynamic properties of these model compounds provide valuable information about solute-solvent and solute-solute interactions, which in turn may help to understand several biochemical processes such as protein hydration, denaturation, aggregation etc. [1-20]. In aqueous medium, amino acids exist essentially as dipolar ions manifesting a unique hydration behaviour, which appears to be subtly linked to the vital biological phenomenon. Because of such subtle linkage, studies of hydration behaviour of amino acids and peptides in different media are also considered of significance in unfolding the role of dipolar ions in the living phenomenon. Moreover,

amino acids are important food additives and have many applications in the pharmaceutical industries, whereas peptides are widely used in drug production that is a result of their ability to act as hormones and their role as signal transmitters in cell communication [21,22].

A literature survey reveals that few attempts [23-28] have been made to evaluate isothermal compressibility (κ_T), for binary liquid mixtures. A number of authors [29-33] have determined the isothermal compressibility values for aqueous solutions of amino acids, peptides and proteins. The data has been discussed in terms of intermolecular/interionic interactions operative in the systems. The knowledge of isothermal compressibility and excess compressibility value may enable one to account for the extent and nature of interactions in mixtures [34, 35, 23, 24]. The excess compressibility values may further be used to evaluate theoretically the sound velocity which describes equilibrium as well as non-equilibrium properties [36].

The ultrasonic velocity and density data of solutions are employed to determine some important thermodynamic parameters such as isothermal compressibility (κ_T), internal pressure (P_i), solubility parameter (δ) and Pseudo-gruneisen parameter (Γ). These parameters impart interesting information about the various interactions operative in solutions.

In continuation of our previous work, [37] we report in this paper the measurements of density and ultrasonic velocity values for ternary systems (amino acid + salt + water): L-isoleucine/L-proline/L-glutamine + K_2SO_4 + water as functions of concentration of amino acid and temperature have been measured. Using the u and ρ data, the κ_T , $P_{i,}$, δ , and Γ values have been computed.

II.EXPERIMENTAL SECTION

The amino acids: L-isoleucine, L-proline and L-glutamine used in this work were obtained from SRL (India). The salt: potassium sulphate was purchased from E. Merck (India). All the chemicals were of $\geq 99\%$ purity. The amino acids were dried at $\sim 110^{\circ}$ C, kept in vacuum desiccator over P₂O₅ for several hours before use. The salts were recrystallized twice in triply distilled water, dried in a vacuum oven and then kept over P₂O₅ in a vacuum desiccator at room temperature for a minimum of 24 hours before use. All the solutions were made by weight using a balance having a resolution of ±0.1mg. Stock solution of 0.5M concentration of K₂SO₄ was prepared in triply distilled water and was used as solvent for the preparation of solutions. The specific conductivity of the water used was less than $18 \times 10^{-6} \Omega^{-1}$ cm⁻¹. Solutions of amino acids of different molal concentration were prepared in aqueous solution of 0.5M K₂SO₄. An ultrasonic interferometer based on variable-path principle was used for the measurement of ultrasound velocity at a frequency of 4 MHz in the temperature range: 303.15 - 323.15K

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by a method described elsewhere [38]. An average of 10 readings were taken as a final value of ultrasound velocity. Water from ultra-thermostat (Type U-10) was circulated through the brass jacket surrounding the cell and the quartz crystal. The jacket was well insulated and the temperature of the solution under study was maintained to an accuracy of $\pm 0.01^{\circ}$. The instrument was calibrated with the triple distilled water. The ultrasonic velocity values of water at different temperatures were taken from literature for calibration purpose [39]. The densities of solutions were measured by pyknometer using a method described elsewhere [38]. The densities of pure water at various required temperatures were taken from literature for calibration purpose [40]. Thermostated water/paraffin bath was maintained at a desired temperature ($\pm 0.01^{\circ}$) for about 30 minutes prior to recording of readings at each temperature of study. Several very close readings recorded at each temperature were averaged.

III.RESULTS AND DISCUSSION

Using the measured u and ρ values, the isothermal compressibility κ_{T1} and κ_{T2} , internal pressure (P_i), solubility parameter (δ), and Pseudo-gruneisen parameter (Γ), values have been computed employing the following relations:

Isothermal compressibility (κ_{T1}) = 1.33x10⁻⁸/(6.4x10⁻⁴ u^{3/2} ρ)^{3/2}

| Isothermal compressit | oility (κ_{T2}) = 17.1x10 | $f^{-4}/T^{4/9} u^2 \rho^{1/3}$ (2) |
|-----------------------|---|-------------------------------------|
| Internal pressure | $P_i = \; (\alpha_T \! / \! \kappa_{T1}) \; \text{-} P$ | (3) |
| solubility parameter | $\delta = (\alpha_T / \kappa_T)$ | $(4)^{1/2}$ |
| Pseudo- gruneisen par | cameter $\Gamma = \gamma - 1/\alpha_{\rm T} T$. | (5) |

The isothermal compressibility values have been computed using the McGowan's [41] expression, replacing the arbitrary constant in the denominator of McGowan's expression by a temperature term, Pandey et al. [42] suggested a relation for the evaluation of isothermal compressibility.

The experimentally measured density values (ρ) for L-isoleucine, L-proline and L-glutamine in aqueous 0.5M K₂SO₄ solution as functions of molal concentration and temperature (303.15, 308.15, 313.15, 318.15 and 323.15) have been listed in Table1.

Table- 1: Density values ($\rho/10^3$ kg m⁻³) as functions of concentration and temperature:

| Concentration | n (mol | Temperature (I | K) | | |
|--------------------|--------|----------------|--------|------------|-------------|
| kg ⁻¹) | - | 303.15 | 308.15 | 313.15 318 | 3.15 323.15 |
| 0.0000 | 1.0593 | 1.0579 | 1.0561 | 1.0542 | 1.0519 |
| 0.0284 | 1.0597 | 1.0582 | 1.0564 | 1.0544 | 1.0521 |
| 0.0474 | 1.0600 | 1.0684 | 1.0565 | 1.0545 | 1.0522 |
| 0.0665 | 1.0603 | 1.0586 | 1.0567 | 1.0546 | 1.0523 |

(I) L-isoleucine in aqueous K₂SO₄ solution

| 0.0857 | 1.0605 | 1.0588 | 1.0569 | 1.0547 | 1.0524 | |
|--------|--------|--------|--------|--------|--------|--|
| 0.1040 | 1.0608 | 1.0500 | 1.0570 | 1.0549 | 1.0525 | |
| 0.1049 | 1.0008 | 1.0390 | 1.0370 | 1.0346 | 1.0325 | |
| 0.1243 | 1.0611 | 1.0592 | 1.0571 | 1.0549 | 1.0526 | |
| 0.1437 | 1.0613 | 1.0593 | 1.0573 | 1.0551 | 1.0527 | |
| 0.1633 | 1.0617 | 1.0596 | 1.0575 | 1.0552 | 1.0528 | |

(II) L-proline in aqueous K₂SO₄ solution

| Concentration | (mol | Temperat | ure (K) | | | |
|--------------------|------|----------|---------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 1.0593 | 1.0579 | 1.0561 | 1.0542 | 1.0519 |
| 0.0953 | | 1.0606 | 1.0592 | 1.0576 | 1.0557 | 1.0534 |
| 0.2909 | | 1.0658 | 1.0643 | 1.0626 | 1.0606 | 1.0584 |
| 0.4934 | | 1.0709 | 1.0694 | 1.0677 | 1.0656 | 1.0633 |
| 0.7032 | | 1.0760 | 1.0745 | 1.0727 | 1.0706 | 1.0683 |
| 0.9206 | | 1.0812 | 1.0796 | 1.0777 | 1.0756 | 1.0733 |
| 1.1462 | | 1.0863 | 1.0847 | 1.0827 | 1.0806 | 1.0782 |

(III) L-glutamine in aqueous K₂SO₄ solution

| Concentration | (mol | Temperate | ure (K) | | | |
|--------------------|------|-----------|---------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 1.0593 | 1.0579 | 1.0561 | 1.0542 | 1.0519 |
| 0.0379 | | 1.0604 | 1.0590 | 1.0573 | 1.0554 | 1.0532 |
| 0.0762 | | 1.0622 | 1.0607 | 1.0590 | 1.0570 | 1.0548 |
| 0.1147 | | 1.0640 | 1.0625 | 1.0607 | 1.0587 | 1.0565 |
| 0.1535 | | 1.0659 | 1.0643 | 1.0624 | 1.0604 | 1.0581 |
| 0.1926 | | 1.0677 | 1.0660 | 1.0641 | 1.0620 | 1.0597 |
| 0.2320 | | 1.0695 | 1.0678 | 1.0658 | 1.0637 | 1.0614 |
| 0.2717 | | 1.0714 | 1.0695 | 1.0675 | 1.0654 | 1.0630 |

The measured ultrasonic velocity values of L-isoleucine, L-proline and L-glutamine in the said aqueous electrolyte solution have been listed in Table 2.

Table-2: Ultrasonic velocity values $(u/m. s^{-1})$ as functions of concentration and temperature:

(I) L-isoleucine in aqueous K_2SO_4 solution

| Concentration (mol | Temperatu | Temperature (K) | | | | |
|--------------------|-----------|-----------------|--------|--------|--------|--|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 | |
| 0.0000 | 1571.2 | 1578.8 | 1587.6 | 1592.6 | 1597.6 | |

| 0.0284 | 1573.8 | 1580.4 | 1589.2 | 1593.6 | 1598.2 |
|--------|--------|--------|--------|--------|--------|
| 0.0474 | 1575.6 | 1582.0 | 1590.6 | 1595.2 | 1599.4 |
| 0.0665 | 1578.0 | 1584.8 | 1592.2 | 1596.4 | 1600.4 |
| 0.0857 | 1579.6 | 1587.7 | 1594.4 | 1598.4 | 1602.8 |
| 0.1049 | 1581.8 | 1590.7 | 1593.4 | 1596.2 | 1601.2 |
| 0.1243 | 1582.1 | 1591.7 | 1595.8 | 1600.4 | 1605.0 |
| 0.1437 | 1585.0 | 1592.0 | 1598.8 | 1604.4 | 1608.4 |
| 0.1633 | 1586.0 | 1593.8 | 1600.8 | 1605.7 | 1609.4 |

(II) L-proline in aqueous K₂SO₄ solution

| Concentration | (mol | Temperat | ure (K) | | | |
|--------------------|------|----------|---------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 1571.2 | 1578.8 | 1587.6 | 1592.6 | 1597.6 |
| 0.0953 | | 1577.2 | 1585.2 | 1592.4 | 1597.2 | 1601.6 |
| 0.2909 | | 1589.2 | 1596.4 | 1604.4 | 1608.6 | 1612.8 |
| 0.4934 | | 1604.2 | 1611.4 | 1618.0 | 1622.4 | 1625.6 |
| 0.7032 | | 1616.0 | 1621.4 | 1625.8 | 1630.4 | 1635.8 |
| 0.9206 | | 1627.2 | 1631.2 | 1634.8 | 1640.2 | 1644.9 |
| 1.1462 | | 1640.4 | 1644.4 | 1648.2 | 1651.8 | 1656.8 |

(III) L-glutamine in aqueous K₂SO₄ solution

| Concentration | (mol | Temperat | ure (K) | | | |
|--------------------|------|----------|---------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 1571.2 | 1578.8 | 1587.6 | 1592.6 | 1597.6 |
| 0.0379 | | 1574.0 | 1581.6 | 1588.6 | 1594.2 | 1598.8 |
| 0.0762 | | 1576.4 | 1585.6 | 1591.2 | 1596.2 | 1601.4 |
| 0.1147 | | 1581.0 | 1588.4 | 1594.8 | 1600.6 | 1605.6 |
| 0.1535 | | 1583.2 | 1590.8 | 1598.4 | 1603.2 | 1607.4 |
| 0.1926 | | 1585.4 | 1592.8 | 1600.0 | 1606.0 | 1610.0 |
| 0.2320 | | 1588.6 | 1596.5 | 1604.4 | 1608.4 | 1613.6 |
| 0.2717 | | 1592.2 | 1598.8 | 1605.0 | 1610.4 | 1614.0 |

The ultrasonic velocity values increase with increase in concentration of amino acids as well as with temperature in all the systems under investigation. The increase in ultrasonic velocity values with increase in concentration for all the systems is almost linear. This increase in ultrasonic velocity values in aqueous amino acids electrolyte solutions may be attributed to the overall increase of cohesion brought about by the solute-solute, solute-

solvent and solvent-solvent interactions in solutions. Amino acids in aqueous solutions essentially behave as zwitter-ions having NH_4^+ and COO⁻ groups at two ends of the molecule. The K⁺, SO₄⁻², ions furnished by electrolyte interact electrostatically with NH_4^+ and COO⁻ groups of amino acid zwitter-ions. In addition, the water dipoles are strongly aligned to the cations/anions as well as to the amino acids zwitter-ions by electrostatic forces. These interactions comprehensively introduce the cohesion into solutions under investigation. The cohesive forces further enhanced on addition of solute molecules in solutions. The added amount of amino acids, zwitter- ions may also occupy the cavities of water clusters which may lead to the formation of denser structure of the aqueous electrolyte solution

The calculated κ_{T1} and κ_{T2} values have been listed in Tables 3 ad 4, respectively.

Table-3: Isothermal compressibility ($\kappa_{T1} \times 10^{12}$, $m^2 N^{-1}$) as functions of concentration and temperature:

(I) L-isoleucine in aqueous K_2SO_4 solution

| Concentration (mol | Temperature (K) | | | | | |
|--------------------|-----------------|--------|--------|--------|--------|--|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 | |
| 0.0000 | 48.48 | 48.05 | 47.57 | 47.36 | 47.10 | |
| 0.0284 | 48.27 | 47.92 | 47.44 | 47.28 | 47.13 | |
| 0.0474 | 48.12 | 47.80 | 47.34 | 47.17 | 47.05 | |
| 0.0665 | 47.94 | 47.59 | 47.22 | 47.08 | 46.98 | |
| 0.0857 | 47.82 | 47.25 | 47.06 | 46.94 | 46.81 | |
| 0.1049 | 47.65 | 47.37 | 47.12 | 46.90 | 46.91 | |
| 0.1243 | 47.60 | 47.22 | 46.96 | 46.80 | 46.65 | |
| 0.1437 | 47.40 | 47.06 | 46.75 | 46.53 | 46.52 | |
| 0.1633 | 47.30 | 46.99 | 46.60 | 46.43 | 46.42 | |
| 0.1633 | 47.30 | 46.99 | 46.60 | 46.43 | 46.42 | |

| () = p | (II) | L-proline in | aqueous | K_2SO_4 | solutio |
|--------|------|--------------|---------|-----------|---------|
|--------|------|--------------|---------|-----------|---------|

| Concentration (mol | Temperatu | re (K) | | | |
|--------------------|-----------|--------|--------|--------|--------|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | 48.48 | 48.05 | 47.57 | 47.36 | 47.19 |
| 0.0953 | 47.97 | 47.53 | 47.21 | 46.96 | 46.82 |
| 0.2909 | 46.82 | 46.44 | 46.03 | 45.89 | 45.82 |
| 0.4934 | 45.51 | 45.15 | 44.84 | 44.70 | 44.65 |
| 0.7032 | 44.45 | 44.21 | 44.05 | 43.90 | 43.72 |
| 0.9206 | 43.45 | 43.31 | 43.21 | 43.01 | 42.87 |
| 1.1462 | 42.37 | 42.23 | 42.13 | 42.04 | 41.90 |

Concentration (mol Temperature (K) kg⁻¹) 303.15 308.15 313.15 318.15 323.15 0.0000 48.48 48.05 47.57 47.36 47.19 0.0379 48.21 47.78 47.42 47,18 47.02 0.0762 47.92 47.40 47.14 46.94 46.74 0.1147 47.49 47.09 46.78 46.54 46.35 0.1535 47.21 46.81 46.44 46.25 46.13 46.95 0.1926 46.57 46.22 45.97 45.86 46.62 0.2320 46.21 45.83 45.71 45.52 0.2717 46.26 45.95 45.68 45.47 45.39

Table- 4: Isothermal compressibility ($\kappa_{T2} \times 10^{12}$, $m^2 N^{-1}$) as functions of concentration and temperature:

| Concentration (mol | Temperature (K) | | | | |
|--------------------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | 50.61 | 49.85 | 49.06 | 48.52 | 48.03 |
| 0.0284 | 50.42 | 49.73 | 48.94 | 48.45 | 47.98 |
| 0.0474 | 50.28 | 49.61 | 48.85 | 48.35 | 47.90 |
| 0.0665 | 50.11 | 49.43 | 48.74 | 48.27 | 47.84 |
| 0.0857 | 50.00 | 49.11 | 43.02 | 48.13 | 47.68 |
| 0.1049 | 49.84 | 49.22 | 48.64 | 48.27 | 47.77 |
| 0.1243 | 49.80 | 49.08 | 48.49 | 48.01 | 47.54 |
| 0.1437 | 49.61 | 48.94 | 48.30 | 47.76 | 47.33 |
| 0.1633 | 49.52 | 48.87 | 48.16 | 47.67 | 47.23 |

(I) L-isoleucine in aqueous K_2SO_4 solution

L-glutamine in aqueous K₂SO₄ solution

(III)

(II) L-proline in aqueous K₂SO₄ solution

| Concentration | (mol | Temperature (K) | | | | |
|--------------------|------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 50.61 | 49.85 | 49.06 | 48.52 | 48.03 |
| 0.0953 | | 50.14 | 49.36 | 48.67 | 48.15 | 47.70 |
| 0.2909 | | 49.07 | 48.36 | 47.64 | 47.18 | 46.79 |
| 0.4934 | | 47.85 | 47.17 | 46.55 | 46.09 | 45.72 |
| 0.7032 | | 46.85 | 46.29 | 45.81 | 45.36 | 44.87 |
| 0.9206 | | 45.91 | 45.45 | 45.03 | 44.54 | 44.10 |
| 1.1462 | | 44.90 | 44.44 | 44.03 | 43.64 | 43.21 |

| Concentration | (mol | Temperature (K) | | | | |
|--------------------|------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 50.61 | 49.85 | 49.06 | 48.52 | 48.03 |
| 0.0379 | | 50.36 | 49.60 | 48.92 | 48.35 | 47.87 |
| 0.0762 | | 50.09 | 49.25 | 48.66 | 48.13 | 47.62 |
| 0.1147 | | 49.69 | 48.96 | 48.33 | 47.77 | 47.27 |
| 0.1535 | | 49.43 | 48.70 | 48.01 | 47.51 | 47.07 |
| 0.1926 | | 49.18 | 48.48 | 47.81 | 47.25 | 46.83 |
| 0.2320 | | 48.88 | 48.15 | 47.45 | 47.01 | 46.52 |
| 0.2717 | | 48.54 | 47.91 | 47.32 | 46.79 | 46.40 |

(III) L-glutamine in aqueous K₂SO₄ solution

The overall trend in the isothermal compressibility has been found to be decreasing with increase in concentration as well as in temperature. The decrease in κ_T values with increase in concentration seems to be the result of a corresponding decrease in free volume. If it is assumed that the size of the ion is not pressure dependent and the electrostricted water is already compressed to its maximum extent by the charge on the ions, the compressibility of a solution is mainly due to the effect of pressure on the bulk water molecules. As the concentration of the electrolyte increases and a large portion of water molecules are electrostricted, the amount of bulk water decreases causing the compressibility to decrease [43]. The decrease in the values of isothermal compressibility with an increase in temperature may be associated with the loss of water molecules around the ions. The calculated isothermal compressibility κ_{T1} , values have been further used for evaluating the internal pressure, solubility parameter and Pseudo-gruneisen parameter. The Internal pressure values of the systems under study have been obtained using the equation [44].

The computed values of P_i are listed in Table 5.

Table- 5: Internal pressure (Pix10⁻⁹, Nm⁻²) as functions of concentration and temperature

(I) L-isoleucine in aqueous K₂SO₄ solution

| Concentration | (mol | Temperatur | e (K) | | | |
|--------------------|------|------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 2.064 | 2.123 | 2.179 | 2.230 | 2.280 |
| 0.0284 | | 2.134 | 2.188 | 2.249 | 2.297 | 2.346 |
| 0.0474 | | 2.199 | 2.254 | 2.316 | 2.367 | 2.415 |
| 0.0665 | | 2.266 | 2.324 | 2.385 | 2.435 | 2.484 |
| 0.0857 | | 2.331 | 2.402 | 2.455 | 2.506 | 2.558 |
| 0.1049 | | 2.399 | 2.457 | 2.515 | 2.562 | 2.618 |
| 0.1243 | | 2.461 | 2.526 | 2.587 | 2.642 | 2.698 |
| 0.1437 | | 2.531 | 2.596 | 2.661 | 2.722 | 2.777 |
| 0.1633 | | 2.596 | 2.661 | 2.732 | 2.792 | 2.843 |

(II) L-proline in aqueous K_2SO_4 solution

| Concentration | (mol | Temperature (K) | | | | |
|--------------------|------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 2.064 | 2.123 | 2.179 | 2.230 | 2.280 |
| 0.0953 | | 1.966 | 2.020 | 1.986 | 2.118 | 2.162 |
| 0.2909 | | 2.066 | 2.120 | 2.177 | 2.222 | 2.266 |
| 0.4934 | | 2.177 | 2.234 | 2.289 | 2.338 | 2.382 |
| 0.7032 | | 2.282 | 2.335 | 2.386 | 2.437 | 2.491 |
| 0.9206 | | 2.388 | 2.439 | 2.488 | 2.544 | 2.598 |
| 1.1462 | | 2.503 | 2.556 | 2.609 | 2.661 | 2.718 |

(III) L-glutamine in aqueous K₂SO₄ solution

| Concentration (mol | Temperatu | Temperature (K) | | | | |
|--------------------|-----------|-----------------|--------|--------|--------|--|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 | |
| 0.0000 | 2.064 | 2.123 | 2.179 | 2.230 | 2.280 | |
| 0.0379 | 2.016 | 2.070 | 2.123 | 2.172 | 2.219 | |
| 0.0762 | 2.084 | 2.145 | 2.196 | 2.244 | 2.294 | |
| 0.1147 | 2.160 | 2.217 | 2.272 | 2.325 | 2.375 | |
| 0.1535 | 2.229 | 2.288 | 2.349 | 2.400 | 2.449 | |
| 0.1926 | 2.359 | 2.421 | 2.483 | 2.542 | 2.593 | |
| 0.2320 | 2.432 | 2.498 | 2.565 | 2.618 | 2.675 | |
| 0.2717 | 2.508 | 2.571 | 2.633 | 2.693 | 2.746 | |

An examination of tables reveals the overall trend in internal pressure has been found to be increasing with increase in temperature, which may apparently be attributed to a decrease in the repulsive forces among the components of the system. The change in concentration of the solution also brings about changes in internal pressure. The change may be attributed to the overall increase of cohesive forces in solutions. It is noteworthy that internal pressure has direct relevance in respect of the force of intermolecular interaction since it happens to be the outcome of such forces per unit area. The increase in the values of internal pressure is closely associated with the expansivity of the system with temperature, as a consequence of which the molecular/ionic species get closer to the extent envisaged by the expansivity of the investigated systems.

The solubility parameter (δ) is obtained by taking the square root of the internal pressure. The calculated values have been presented in Table 6.

Table-6: Solubility parameter, $\delta \propto 10^{-4}$, $(Nm^{-2})^{1/2}$ as functions of concentration and temperature:

(I) L-isoleucine in aqueous K_2SO_4 solution

Concentration (mol Temperature (K)

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| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
|--------------------|--------|--------|--------|--------|--------|
| 0.0000 | 4.543 | 4.608 | 4.668 | 4.722 | 4.775 |
| 0.0284 | 4.619 | 4.677 | 4.743 | 4.793 | 4.844 |
| 0.0474 | 4.689 | 4.747 | 4.813 | 4.865 | 4.915 |
| 0.0665 | 4.761 | 4.821 | 4.883 | 4.934 | 4.984 |
| 0.0857 | 4.829 | 4.901 | 4.955 | 5.006 | 5.058 |
| 0.1047 | 4.898 | 4.957 | 5.015 | 5.062 | 5.117 |
| 0.1243 | 4.960 | 5.026 | 5.086 | 5.140 | 5.194 |
| 0.1437 | 5.031 | 5.095 | 5.159 | 5.217 | 5.270 |
| 0.1633 | 5.095 | 5.159 | 5.227 | 5.284 | 5.332 |

(II) L-proline in aqueous K₂SO₄ solution

| Concentration | (mol | Temperature (K) | | | | |
|--------------------|------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 4.543 | 4.608 | 4.668 | 4.722 | 4.775 |
| 0.0953 | | 4.434 | 4.495 | 4.456 | 4.602 | 4.650 |
| 0.2909 | | 4.545 | 4.604 | 4.665 | 4.714 | 4.760 |
| 0.4934 | | 4.666 | 4.726 | 4.784 | 4.835 | 4.881 |
| 0.7032 | | 4.778 | 4.832 | 4.884 | 4.936 | 4.991 |
| 0.9206 | | 4.886 | 4.938 | 4.988 | 5.044 | 5.097 |
| 1.1462 | | 5.003 | 5.056 | 5.108 | 5.199 | 5.214 |

(III) L-glutamine in aqueous K₂SO₄ solution

| Concentration | (mol | Temperature (K) | | | | |
|--------------------|------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | 4.453 | 4.608 | 4.668 | 4.722 | 4.775 |
| 0.0379 | | 4.490 | 4.550 | 4.608 | 4.661 | 4.710 |
| 0.0762 | | 4.566 | 4.632 | 4.686 | 4.738 | 4.790 |
| 0.1147 | | 4.648 | 4.709 | 4.766 | 4.822 | 4.874 |
| 0.1535 | | 4.721 | 4.784 | 4.846 | 4.899 | 4.949 |
| 0.1926 | | 4.857 | 4.920 | 4.983 | 5.041 | 5.092 |
| 0.2320 | | 4.932 | 4.998 | 5.064 | 5.116 | 5.172 |
| 0.2717 | | 5.008 | 5.070 | 5.131 | 5.189 | 5.240 |

These values have been found to increase in temperature. Such an increase may be attributed to an increase in the cohesive energy density. The trend of variation of δ with the said amino acid concentration and temperature is similar to that of internal pressure since it is the square root of P_i. There is also a significant change in solute concentration when the systems have been examined keenly at different temperatures.

The pseudo-gruneisen parameter (Γ), which happens to be a measure of the degree of molecular/ionic association has been evaluated where γ is the specific heat ratio obtained from the relation, $\gamma = C_P/C_V = \kappa_{T1}/\kappa_s$. The calculated Γ values have been listed in Table 7.

Table- 7: Pseudo-Gruneisen parameter (Γ) as functions of amino acid concentration and temperature: (I) L-isoleucine in aqueous K₂SO₄ solution

| Concentration (mol | Temperature (K) | | | | | | |
|--------------------|-----------------|--------|--------|--------|--------|--|--|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 | | |
| 0.0000 | -8.729 | -8.562 | -8.426 | -8.269 | -8.115 | | |
| 0.0284 | -8.480 | -8.330 | -8.185 | -8.040 | -7.898 | | |
| 0.0474 | -8.254 | -8.108 | -7.964 | -7.824 | -7.686 | | |
| 0.0665 | -8.039 | -7.896 | -7.757 | -7.619 | -7.484 | | |
| 0.0857 | -7.835 | -7.696 | -7.560 | -7.426 | -7.294 | | |
| 0.1049 | -7.642 | -7.505 | -7.371 | -7.240 | -7.112 | | |
| 0.1243 | -7.458 | -7.324 | -7.193 | -7.065 | -6.940 | | |
| 0.1437 | -7.282 | -7.151 | -7.023 | -6.898 | -6.776 | | |
| 0.1633 | -7.116 | -6.987 | -6.862 | -6.739 | -6.619 | | |
| | | | | | | | |

(II) L-proline in aqueous K₂SO₄ solution

| Concentration | (mol | Temperature (K) | | | | |
|--------------------|------|-----------------|--------|--------|--------|--------|
| kg ⁻¹) | | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | | -8.729 | -8.562 | -8.426 | -8.269 | -8.115 |
| 0.0953 | | -9.260 | -9.098 | -8.934 | -8.784 | -8.628 |
| 0.2909 | | -9.037 | -8.879 | -8.724 | -8.570 | -8.419 |
| 0.4934 | | -8.827 | -8.672 | -8.520 | -8.370 | -8.222 |
| 0.7032 | | -8.628 | -8.476 | -8.327 | -8.180 | -8.035 |
| 0.9206 | | -8.440 | -8.291 | -8.144 | -8.000 | -7.859 |
| 1.1462 | | -8.262 | -8.116 | -7.971 | -7.830 | -7.692 |

(III) L-glutamine in aqueous K_2SO_4 solution

| Concentration (mol | Temperatu | re (K) | | | |
|--------------------|-----------|--------|--------|--------|--------|
| kg ⁻¹) | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| 0.0000 | -8.729 | -8.562 | -8.426 | -8.269 | -8.115 |
| 0.0379 | -8.985 | -8.828 | -8.674 | -8.522 | -8.372 |
| 0.0762 | -8.745 | -8.592 | -8.441 | -8.292 | -8.147 |
| 0.1147 | -8.518 | -8.369 | -8.221 | -8.077 | -7.935 |
| 0.1535 | -8.304 | -8.158 | -8.014 | -7.873 | -7.733 |

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|---|--------|--------|--------|--------|-------------------------|--|--|
| 0.1926 | -7.893 | -7.753 | -7.616 | -7.481 | -7.349 | | |
| 0.2320 | -7.710 | -7.574 | -7.439 | -7.307 | -7.178 | | |
| 0.2717 | -7.537 | -7.402 | -7.270 | -7.142 | -7.015 | | |

The decrease in values with increase in temperature may apparently be attributed to an increase in the kinetic energy of molecules, which in turn, increase the thermal motion of molecules and disrupts the molecular association. The Γ values also show a decreasing trend of variation with increase in amino acid concentration in aqueous electrolytic solutions. However it may be noted that such a variation with change in concentration of solute is insignificant.

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REFERENCES

- TH Lilley, in Biochemical Thermodynamics, MN Jones (ed.), Elsevier: Amsterdam 1988.
- [2]. F Franks, in Biochemical Thermodynamics, MN Jones (ed.), Elsevier: Amsterdam 1988.
- [3]. DP Kharakoz. Journal of Physical Chemistry 95,1991, 5634.
- [4]. DP Kharakoz. Biophysical Chemistry 34, 1989, 115.
- [5]. GR Hedwig and H Hoiland. Journal of Chemical Thermodynamics 23, 1991,1029.
- [6]. GR Hedwig and H Hoiland. Journal of Chemical Thermodynamics25,1993,349.
- [7]. GR Hedwig. Journal of Chemical Society Faraday Transactions 1993, 2761.
- [8]. M Sahayam and GR Hedwig. Journal of Chemical Thermodynamics 26, 1994, 361.
- [9]. GI Makhatadze and PL Privalov. Journal of Molecular Biology 213, 1990, 375.
- [10]. R Bhat and JC Ahluwalia. Journal of Physical Chemistry 89, 1985, 1099.
- [11]. TV Chalikian, AP Sarvazyan and KJ Breslauer. Journal of Physical Chemistry 97,1993, 13017.
- [12]. OP Chimankar, R Shriwas and VA Tabhane. Journal of Chemical Pharmaceutical Research 3,2011, 587.
- [13]. S Mirikar, PP Pawar and GK Bichile. Journal of Chemical Pharmaceutical Research 3,2011, 306.
- [14]. M Iqbal and T Ahmed. Indian Journal of Chemistry 32A, 1993, 119.
- [15]. MP Breil, JM Mollerup, E Susanne, J Rudolph, M Ottens and LA M Van der Wielen. Fluid Phase Equilibria215,2004,221.
- [16]. BH Park, KP Yoo and CS Lee. Fluid Phase Equilibria 212, 2003, 175.

- [17]. OP Chimankar, RS Shriwas, PS Chopade and VA Tabhane. Journal of Chemical Pharmaceutical Research 3,2011, 579.
- [18]. JP Amend and HC Helgeson. Biophysical Chemistry 84,2000, 2000,105.
- [19]. EL Shock. Geochim. Cosmochimica Acta 56,1992, 3481.
- [20]. M Häckel, HJ Hinz and GR Hedwig. Thermochimica Acta 308,1998,23.
- [21]. H Rodriguez, A Soto, A Arce and MK Khoshkbarchi. Journal of Solution Chemistry 32,2003,53
- [22]. A Soto, A Arce and MK Khoshkbarchi. Journal of Solution Chemistry 33,2004,11.
- [23]. JD Pandey and K Misra. Acoustic Letters 6,1983, 1983,148.
- [24]. DD Despande and LG Bhatgadde. Journal of Physical Chemistry 72, 1963,261.
- [25]. LG Bhatgadde, S Oswal and CS Prabhu. Journal of Chemical Engineering Data 19,1971,469.
- [26]. BP Shukla and SN Dubey. Acoustic Letters 9,1985,71.
- [27]. FJ Millero, GK Ward and P Chetirkin. J. Biophysical. Chemistry 251, 1976, 4001.
- [28]. AA Yayanos. Journal of Physical Chemistry 97, 1993, 13027.
- [29]. AFSS Mendonca, SMA Dias, FA Dias, BAS Barata and IMS Lampreia. Fluid Phase Equilibria 212,2003,67.
- [30]. AP Sarvazyan, DP Kharakoz and P Hemmas. Journal of Physical Chemistry 83, 1979, 1796.
- [31]. AW Hain, H Hoiland and GR Hedwig. Physical Chemistry of Chemical Physics 2,2000, 4850.
- [32]. FJ Millero, GK Ward, FK Lepple and EV Hoff. Journal of Physical Chemistry 78, 1974,1636.
- [33]. JD Pandey, BR Chaturvedi and N Pant. Acoustic Letters 4,1980, 92.
- [34]. MR Islam and SK Quadri. Acoustic Letters 11,1988,219.
- [35]. JD Pandey, GP Dubey, BP Shukla and SN Dubey Acustica 80,1994,92.
- [36]. JO Hirschfeider, CF Curtiss and RB Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, Inc.: New York 1957, 286.
- [37]. Riyazuddeen and R Basharat. Journal of Chemical Thermodynamics 38, 2006,1684.
- [38]. S Islam and BN Waris. Thermchimica Acta 424, 2004, 165.
- [39]. VA Del Grosso and CW Mader. Journal of Acoustic Society of America 52, 1972,1442.
- [40]. GS Kell. Journal of Chemical Engineering Data 20,1975,97.
- [41]. JC McGown. Nature (London), 210, 1966,1255.
- [42]. JD Pandey, Vyas, Pramana. Journal of Physics 43, 1994, 36.
- [43]. FJ Millero, RW Curry, W Drost-Hansen. Journal of Chemical Engineering Data 14,1969, 422.
- [44]. MR Islam and SK Quadri. Acoustic Letters 12, 1988,219.