International Journal on Science and Technology (IJSAT)
E-ISSN: 2229-7677 ● Website: www.ijsat.org ● Email: editor@ijsat.org

Isothermal Compressibilities, Internal Pressures, Solubility Parameters and Pseudo- Gruneisen Parameters Of L-Isoleucine, L-Proline and L-Glutamine in Aqueous K2SO4, KNO3 and KCI Solutions

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1. Introduction

Proteins, large molecules with high molecular weights are composed of varying amount of essentially the same about twenty amino acids well known for this purpose. Proteins play a vital role in nearly all the biological processes. Every protein has a unique three-dimensional structure that may reflect its envisaged function. Its structure is known to be stabilized by the presence of multiple weak interactions. Hydrophobic interactions provide the major contribution to stabilizing the globular form of most soluble proteins; hydrogen bonds and ionic interactions are optimized in the specific structure that is thermodynamically most stable. The thermodynamic stability of the native structure of protein has provided one of the great challenges in Biophysical Chemistry and Biophysics; and still currently remains the subject of extensive investigations (1-14).

The knowledge of stability of proteins in aqueous and mixed aqueous solutions is essential for understanding their structures and functions. The stability of a globular protein in aqueous solutions can be determined by studying the disruption of its native structure, i.e., the process of denaturation. The denaturation of globular proteins in aqueous solutions is a fundamental biological process. During this process, the native folded conformation of protein is converted predominantly into an extended unfolded form and during this process various changes occur in protein hydration. Protein hydration that is the interaction of water with various functional groups of proteins is an important factor in determining the conformational stability of proteins (8-10). Thus, the thermodynamic studies of native and denatured states of proteins are necessary to understand the role of hydration in protein folding / unfolding processes (15-17). The structural details revealed by the high-resolution x-ray crystallography, neutron diffraction, spectroscopy and thermodynamic methods have contributed a great deal towards our understanding of protein functions (18).

The amino acids, the alphabet of protein structure, can be arranged in an almost infinite number of sequences to make an almost infinite number of different proteins. Amino acids are characterized by the presence of a carboxyl group (-COOH) and an amino group (-NH2) attached to the same carbon at the end of the compound. Every amino acid except glycine can occur as either of the optically active

stereoisomers, D or L; the more common isomer in nature is the L-form. When the carboxyl carbon atom of one amino acid covalently binds to the amino nitrogen atom of another amino acid with the release of water molecule, a peptide bond is formed. Asparagine was the first amino acid to be discovered in proteins in 1806.

The direct interpretation of thermodynamic studies on complex configurational and conformational structure of proteins in various solvents is rather tedious and difficult. Therefore, investigations of the behaviour of protein model compounds: amino acids and peptides are of importance. Amino acids and peptides, the basic molecular building blocks of proteins, have been often used as the most conventional substances to estimate the individual contribution of monomeric units in proteins (19). Thermodynamic studies of amino acids and peptides are also helpful in understanding the phase equilibria and separation behaviour of these compounds (20). The thermodynamic properties of amino acids and peptides in aqueous medium provide information about the solute-solvent and solute-solute interactions which, in turn, may be employed to understand several biochemical processes such as protein hydration, denaturation, aggregation, etc. (4,14,18,19,21-103).

The interaction of electrolytes with biochemical compounds have been the subject of numerous studies (104), but little attention has been paid to the properties of aqueous amino acid – electrolyte solution (20,27,92,105-118) despite their physiological importance. A quantitative analysis of the effect of electrolytes on amino acids and peptides is desirable in view of both, theoretical as well as practical applications. The addition of amino acid to electrolytes brings about a sharp change in the solvation of ions. Amino acids form hydrogen bonds with water but in presence of electrolytes it has been observed that there is a complete loss of structure due to bonding between water and the added electrolyte. The change in the structure of solvent or solution around the solute molecule /ion as a result of hydrogen bond formation or disruption leads to decrease or increase in intermolecular free length. It is useful to extend the study of amino acids to a mixed solvent system not only because of the fact that the mixed aqueous solvents are used extensively in chemistry and other related fields to control the factors, which affect some of the properties of significance such as solubility, reactivity and stability of systems but also because biological fluids are ultimately not pure water.

A number of physical techniques have so far been employed to study the intermolecular / interionic interactions in aqueous and non-aqueous systems, but no method alone provide a complete understanding of the nature of these interactions. The density, viscosity and ultrasonic velocity studies of solutions have been employed for studying the behaviour of biological macromolecules. These studies enable one to investigate and understand the inherent concept of the intermolecular interactions and to correlate their behaviour with thermodynamic properties.

Ultrasonic velocity technique has been used to study the thermodynamic properties of aqueous and non-aqueous systems (39,57,64,111,112,116,119-138). The velocity data along with those of density can be employed for the computation of various thermodynamic parameters, namely, isentropic compressibility, change and relative change in isentropic compressibility, specific acoustic impedance and relative association to provide a better source of understanding of interionic / intermolecular interactions in solutions. Nomoto in 1958 (139) and Bhimsenachar et al. in 1962 (140) proposed the relations to evaluate theoretically the sound velocity in liquid mixtures. The ideal mixing relation for ultrasound velocity has been applied by Van Dael and Vangeel (141). Schaffs (142) and Nikan et al. (143) have shown that the sound velocity in the liquid mixture is proportional to the space-filling factor.

In addition, the Flory-Patterson theory has also been attempted to evaluate theoretically the ultrasonic velocity of liquid mixtures using the reduced and characteristic parameters of pure liquids (144,145).

Isothermal compressibility, a thermodynamic parameter, provides a better understanding of the interactions in solutions. Various attempts have been made to evaluate the isothermal compressibility of binary liquid mixtures as well as of aqueous electrolyte solutions (146-157). Chaturvedi and Pratap (158) employed the Carnahan and Starling (151); and Thiele (150) equations to obtain the isothermal compressibility and related properties of a number of liquids at room temperature. Some hard sphere models have also been used to obtain the isothermal compressibility and related thermodynamic parameters of liquids (159-162). McGown (163) and Pandey et al. (164) proposed direct methods for the calculation of isothermal compressibility using the ultrasonic velocity and density data.

The role of internal pressure in liquid thermodynamics was recognized many years ago by Hildebrand (165) following earlier work of Van Laar (166). Pioneer attempts have been made by Barton (167,168), Cagle (169), Rosseinsky (170), Berkowitz et al. (171), Hildebrand et al. (172-174) and Liberman (175) to show the significance of internal pressure as a fundamental property of liquid state and its correlation with other properties. Dunlop et al. (176) determined the internal pressure of different liquid mixtures and compared it with their cohesive energy density values. Suryanarayana (177) suggested an indirect method of evaluating internal pressure from the data of viscosity, density and ultrasonic velocity. This approach has been extensively used for studying the internal pressure of pure liquids, binary liquid mixtures, and solutions of electrolytes and non-electrolytes (178). In addition, properties of liquids such as solubility (179), surface tension (179), energy of activation of viscous flow, dipole moments (180), the glass transition in polymers (181,182) and viscosity properties of polymers (183,184) have been discussed widely in terms of internal pressure, cohesive energy density and solubility parameter values.

The square root of the cohesive energy density is referred to as solubility parameter. This property has been extensively discussed in a review presented by Barton (168). The “universality” of the solubility parameter into parts representing dispersion, dipole-dipole and hydrogen bonding cohesion energies permits a wide use of this parameter (185-187). Pseudo-Gruneisen parameter, a dimensionless constant is governed by the molecular order and structure. Lattice order of liquids can be revealed in the light of this parameter.

Volumetric properties such as apparent / partial molal volumes of solutes in solution can provide better information about the various types of ionic/molecular interactions, viz. hydrogen bonding (188,189), electrostriction (190,191), ionization (192,193), hydrophobic/ hydrophilic interactions (190), and zwitterions formation (74). A number of researchers have determined the partial molal volume of a variety of solutes in different solvents in order to study the solute-solvent interactions in solutions (32-34,36,41,42,45-48,60,62,72,92,105-110,113,115,117,194-202). In addition, partial molal volume measurements are important for obtaining information about the hydration phenomena of solute in a solution (23).

Partial molal isentropic compressibility of solution is an essential physical characteristic reflecting intermolecular/interionic interactions. Studies of compressibility of aqueous solutions of proteins have started a long time ago (203,204). During the last decade a new approach has been developed for investigation of protein volume and compressibility based on x-ray analysis (205-207). In 1964, Goto and Isemura measured the apparent isentropic compressibility of fourteen amino acids over a

temperature range from 15 to 45°C (63). Millero et al. (64) have studied fifteen amino acids in aqueous solutions at 25°C. The partial molal isentropic compressibility of a protein in aqueous solution can be considered to be made up of essentially two terms (208,209). One contribution is from the intrinsic compressibility of a protein, which arises from the void volume that exists within the molecule due to imperfect packing of protein chain. The second contribution is due to the hydration of the various amino acid residues that are exposed to the solvent.

Viscometric studies are important for studying transport properties of pure and mixed solutions. Viscosity has been found to be a measure of the resistance of a fluid to flow. The increase in viscosity due to the presence of particles arises from the fact that they lie across the fluid streamlines and are subject to torsional forces. They tend to rotate and then absorb energy. This energy absorption leads to an increased viscosity of the solution (56). It has been observed that viscous forces appear only when adjacent parts of a fluid are moving with different velocities.

The viscosity derived parameters, such as specific, reduced and intrinsic viscosities provide a better understanding of intermolecular / interionic interactions in solutions (54,210-219). The solute-solvent interactions can also be studied in terms of B-coefficient of Jones-Dole equation (220). The partitioning of the B-coefficient into their ionic components was first proposed by Cox and Wolfenden (221) and it was re-examined by Gurney (222) and Kaminsky (223) in 1965. Martin and Tsangaris (55) in 1965 studied the structure making / breaking effects of amino acids on water in terms of B-coefficient and its temperature derivative, dB/dT, values. They found that the magnitude of dB/dT values is more important than the B-coefficient for explaining the structure making / breaking effects of amino acids on water.

It appears, however, from the exhaustive literature survey that a number of thermodynamic properties of amino acids have been studied in aqueous medium (52,61,83,224-226) but few authors have attempted to investigate amino acids in aqueous electrolyte solutions as functions of concentration and temperature (35,82,227-229). Consequently, with a view to understanding the intermolecular / interionic interactions of amino acids, namely L-isoleucine, L-proline and L-glutamine in 0.5M potassium sulphate, 1M potassium nitrate and 1.5M potassium chloride aqueous solutions, the densities, ultrasonic velocities and viscosities have been measured as functions of temperature and concentration.

Experimental

Material And Sample Preparation

The amino acids: L-isoleucine, L-proline and L-glutamine of high purity (≥99%) used in the studies were obtained from Sisco Research Laboratories, India. All the three amino acids were used without further purification. The amino acids were dried at ~110°C and stored in a vacuum desiccator for several hours before use. The electrolytes KNO3 and KCl were obtained from E. Merck, India; and K2SO4 from S.D. Fine, India. These salts were of high purity (≥99%). The salts were recrystallized in triple distilled water and were dried at 110°C and then kept in vacuum desiccator for several hours. Stock Solutions of 0.5 M K2SO4, 1 M KNO3 and 1.5 M KCl were prepared in triple distilled water and used as solvents for the preparation of solutions. Water used in the experiments was deionized, triple-distilled, and was degassed prior to making solutions. The degree of degassing was sufficiently high to

prevent formation of bubbles in the measuring cell. All the solutions were made by weight on the molality concentration scale within an accuracy of $\pm 1\times10^{-4}$ mol Kg^{-1}.

Temperature Control

A thermostated paraffin bath was used to maintain the desired temperature during the measurements of density and viscosity. The bath was made up of an immersion heater (1.5 KW), a stirrer, a check thermometer (Germany), a contact thermometer and a relay [Jumo type, NT 15.0, 220 V ≅ 10A (Germany)]. Thermal stability of the thermostat was found to be within ± 0.1°.

Density Measurement

Pyknometer consisting of a small bulb with flat bottom of approximately 3.5 ml capacity and a graduated stem was used for the density measurements. The volume at each mark of the pyknometer was calibrated with triple distilled water. The densities of pure water at various required temperatures were taken from literature for calibration purpose (230). In order to check the reproducibility of calibration, the same process was repeated a number of times with different amounts of water. The reproducibility of density values was found to be within ± 0.0003 gm/cm^3. The test solution was introduced into the calibrated pyknometer, weighed and then it was immersed in the paraffin bath. By recording the volume changes as a function of temperature, the densities of solutions were determined at required temperatures.

Viscosity Measurement

Canon-Fenske viscometer was used for the viscosity measurement of various solutions under study. The viscometer consists of three parallel arms with a common base. The viscometer was calibrated with the triple distilled water. The viscosity coefficient values of water at different temperatures were taken from literature (231). The clean and dry viscometer was filled with test solution and was clamped in the thermostated bath in a vertical position. In order to avoid the absorption of moisture by solution, the open ends of the three arms of viscometer were fitted with the anhydrous calcium chloride glass tubes through rubber tubes. The solution was sucked into the measuring bulb and was allowed to stand there for about two minutes by closing the calcium chloride tubes with rubber corks and then the corks were removed for recording the time of fall of solution from the upper to lower end of the bulb. After taking several readings at the desired temperature the average of the very close values of time of fall was taken.

The viscosity coefficient was calculated employing the following Poiseuille's equation,

$$\eta = \pi gh\ \rho tr^4/8vl \qquad [1]$$

where g, h, ρ, r, l and t are acceleration due to gravity, height of the column in the viscometer, density of the liquid, radius of the viscometer's capillary, length and time of fall for the liquid of volume v through the capillary, respectively. The above equation can also be written as

$$\eta = \rho\beta t \qquad [2]$$

where $\beta = \pi ghr^4/8vl$ is constant for a given viscometer. The viscosity value of the test solution was calculated using the reported viscosity values of pure water at various temperatures. Equation [3] was employed for the calculation of viscosity of solutions.

$$\eta_1 = (\rho_1 t_1 / \rho_2 t_2) \times \eta_2 \qquad [3]$$

where η, ρ and t are the viscosity coefficient, the density and the time of fall of the solution, respectively. The reproducibility in viscosity measurements was found to be within $\pm 0.003 \times 10^{-4}$ N m^{-2} s.

Ultrasonic Velocity Measurement

An ultrasonic interferometer (Mittal's model: M-77) was used for the measurement of ultrasound velocity at a frequency of 4 MHz in the temperature range: 298.15 – 323.15 K. 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 ± 0.1°. The instrument was calibrated with the triple distilled water. The ultrasonic velocity values of water at different temperatures were taken from literature (232) for calibration purpose.

Working Principle

An ultrasonic interferometer is a simple and direct device to determine the ultrasonic velocity in liquids with a high degree of accuracy. The principle used in the measurement of velocity (u) is based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic waves of known frequency (f) are produced by a quartz plate fixed at the bottom of the cell. A movable metallic plate kept parallel to the quartz plate reflects these waves. If the separation between these two plates is exactly a whole multiple of the ultrasound wavelength, standing waves are formed in the medium. This acoustic resonance gives rise to an electrical reaction on the generator driving the quartz plate and the anode current of the generator becomes maximum. If the distance is now increased or decreased and the variation is exactly one half wavelength ($\lambda/2$) or multiple of it, anode current again becomes maximum. The velocity can be obtained by using the relation,

$$u = \lambda \times f \qquad [4]$$

Description

The ultrasonic interferometer consists of two parts (i) the high frequency generator and (ii) the measuring cell. The “high frequency generator” is designed to excite the quartz plate fixed at the bottom of the measuring cell and its resonant frequency to generate ultrasonic waves in the liquid filled in the “measuring cell”. A micrometer to observe the change in current and two controls for the purpose of sensitivity regulation and initial adjustments of micrometer are provided on the panel of the high frequency generator. The “measuring cell” is a specially designed double walled cell for maintaining a constant temperature of the liquid during experiment. A fine micrometer screw has been provided at the top, which can lower or raise the reflector plate in the liquid in the cell through a known distance. It has quartz plate fixed at its bottom.

Instrument was adjusted in the following manner:

1. The cell was inserted in the square base socket and clamped to it with the help of a screw provided on one of its sides.
2. The curled cap of the cell was unscrewed and removed from the double walled construction of the cell. In the middle portion of it the experimental liquid was poured and screwed the curled cap.
3. Water was circulated through the two chutes in the double wall construction in order to maintain the desired temperature.
4. The cell was connected with the high frequency generator by a co-axial cable provided with the instrument.

For the initial adjustment, two knobs are provided on high frequency generator, one is marked with 'Adj' and the other with 'Gain'. With knob marked 'Adj' the position of needle on the ammeter was adjusted and the knob marked 'Gain' was used to increase the sensitivity of the instrument for greater deflection. The ammeter was used to record the maximum deflections by adjusting the micrometer.

Measurements

The measuring cell was connected to the output terminal of the high frequency generator through a shielded cable. The cell was filled with the liquid before switching on the generator. The ultrasonic waves of 4 MHz frequency produced by a gold plated quartz crystal fixed at the bottom of a cell are passed through the medium. A movable plate reflects the waves and the standing waves are formed in the liquid in between the reflector plate and the quartz crystal. Acoustic resonance due to these standing waves gives rise to an electrical reaction to the generator driving the quartz plate and the anode current of the generator becomes maximum. The micrometer screw was raised slowly to record the maximum anode current. The wavelength was determined with the help of a total distance moved by the micrometer for twenty maximum readings of the anode current. The total distance (d) gives the value of wavelength with the help of the relation, $d = n \times \lambda/2$, where n is the maximum number of readings. Using the wavelength, the ultrasound velocity in the liquid was obtained with the help of Equation [4]. The reproducibility in velocity measurement was within $\pm$ 0.5 ms^{-1}.

Precautions

1. The generator was switched on after filling the cell by the experimental liquid.
2. The experimental liquid was removed from the cell after use.
3. The micrometer was kept open at 25 mm after use.
4. The sudden rise or fall in the temperature of circulated liquid was avoided to prevent thermal shock to the quartz crystal.
5. While cleaning the cell, care was taken not to spoil or scratch the gold plating on the quartz crystal.
6. The generator was given 15 minutes warming up time before observation.

The ultrasonic velocity and density data of solutions are employed to detennine some additional thermodynamic parameters such as isothermal compressibility (KT), internal pressure (Pj), solubility parameter (5) and Pseudo-Gruneisen parameter (F). Isothermal compressibility is an important thermodynamic parameter and has been widely evaluated by many workers (146-157) using several equations of state for pure and mixed liquids; and melts. The knowledge of this parameter may enable one to account for the extent and nature of interactions in solutions. Many researchers (52,53,249,250) have employed the isothermal compressibility data for elucidating the intermolecular interactions in amino acids and proteins in aqueous medium. Internal pressure has been found to be a useful parameter for studying the solute-solvent interactions of bio-molecules in aqueous medium (247). This has been applied in the cases of liquids and liquid mixtures initially by Hildebrand et al. (251,252) and subsequently by several workers (167,177,253-257). Internal pressure turns out to be a measure of the totality of forces including dispersion, repulsion, ionic and dipolar interactions that contribute to the overall cohesion in electrolyte and non-electrolyte aqueous solutions and liquid mixtures. Another parameter, known as the solubility parameter has been employed for assessing the compressibilities of various substances and for selecting the proper compounding ingredients (258), and solvents for polymeric substances (259) and paints (260). Hildebrand and Scott (172, 251) introduced this parameter in the theory of solutions. Several workers (168,261) have used the solubility parameter to measure the cohesive energy density of solutions. The Pseudo-Gruneisen parameter has been extensively used by a number of workers (261-268) for investigating the anharmonic properties of liquids. Pseudo-Gruneisen parameter has also been employed to study the thermodynamic behaviour of liquid systems (269,270). RESULTS AND DISCUSSION Isothermal compressibility of amino acids, namely, L-isoleucine, L-proline, and L-glutamine in aqueous K2SO4, KNO3 and KCl solutions have been computed using the McGowan's (163) expression, KT, = I.33xl0-V (6.4xl0"' u^^" p)^'^ [2.1] where u and p are the experimental ultrasonic velocity and density data, respectively. Replacing the arbitrary constant in the denominator of McGowan's expression by a temperature term, Pandey et al. (164) suggested a relation for the evaluation of isothermal compressibility, KT2-=17.1X10'V%'P'-' [2.2]. The calculated KJI and KT2 values have been listed in Tables 2.1 and 2.2, respectively. These values of KTI and K]2 ha\c been found to decrease with increase in concentration of amino acids in aqueous elcctrolMic solutions. The decrease in KJ values with increase in concentration seems to be the result of a corresponding decrease in free volume. The KH and KT2 values also show decreasing trend with increase in temperature. This trend of variation may be attributed to the formation of smaller

Table 2.1: Isothermal compressibility (KTIXIO , m N") as functions of concentration and temperature

(i) L-isoIeucine in aqueous K2SO4 solution

Concentration	298.15	303.15	308.15	313.15	318.15	323.15
0.0000	48.90	48.48	48.05	47.57	47.36	47.19
0.0284	48.81	48.27	47.92	47.44	47.28	47.13
0.0474	48.52	48.12	47.80	47.34	47.17	47.05
0.0665	48.47	47.94	47.59	47.22	47.08	46.98
0.0857	48.20	47.82	47.25	47.06	46.94	46.81
0.1049	48.15	47.65	47.37	47.12	46.90	46.91

0.1243	48.10	47.60	47.22	46.96	46.80	46.65
0.1437	47.89	47.40	47.06	46.75	46.53	46.52
0.1633	47.74	47.30	46.99	46.60	46.43	46.42

(ii) L-isoIeucine in aqueous KNO3 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	51.69	51.04	50.55	50.18	49.90	49.73
0.0285	51.64	50.95	50.45	50.10	49.85	49.68
0.0477	51.51	50.84	50.35	50.01	49.77	49.64
0.0669	51.27	50.71	50.25	49.94	49.70	49.59
0.0862	50.98	50.40	49.99	49.85	49.66	49.49
0.1056	50.82	50.20	49.83	49.68	49.39	49.28
0.1250	50.61	50.07	49.77	49.55	49.13	49.08
0.1446	50.46	49.98	49.70	49.32	49.02	48.95
0.1642	50.33	49.79	49.45	49.24	48.92	48.88

(iii) L-isoleucine in aqueous KCI solution

Concentration	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	47.46	47.14	46.91	46.68	46.53
0.0284	47.30	47.05	46.88	46.61	46.46
0.0474	47.26	47.00	46.84	46.56	46.40
0.0665	47.18	46.90	46.76	46.45	46.34
0.0856	47.04	46.76	46.62	46.39	46.29
0.1049	46.80	46.52	46.39	46.33	46.20
0.1243	46.71	46.41	46.26	46.19	45.98
0.1437	46.51	46.34	46.10	45.92	45.82
0.1632	46.34	46.18	45.99	45.77	45.67

(iv) L-proline in aqueous K2SO4 solution

Concentration	**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

(v) L-proline in aqueous KNO3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	51.04	50.55	50.18	49.90	49.73
0.0958	50.33	50.22	49.88	49.64	49.46
0.1932	49.81	49.62	49.41	49.19	49.02
0.2923	49.24	49.02	48.70	48.55	48.37
0.3932	48.85	48.61	48.30	47.95	47.89
0.4958	48.22	47.87	47.69	47.49	47.38
0.6002	47.42	47.29	46.98	46.73	46.74
0.7065	46.96	46.83	46.44	46.26	46.23
0.8146	46.56	46.29	46.00	45.88	45.69
0.9248	45.82	45.51	45.33	45.25	45.16
1.0371	45.34	45.11	45.11	44.96	45.14

(vi) L-proline in aqueous KCI solution

Concentration	298.15	303.15	308.15	313.15	318.15	323.15
0.0000	47.82	47.46	47.14	46.91	46.68	46.53
0.0950	47.60	47.18	46.82	46.47	46.21	46.11
0.2900	46.58	46.06	45.66	45.42	45.27	45.13
0.4920	45.39	44.89	44.67	44.42	44.33	44.26
0.7015	44.22	43.92	43.60	43.45	43.38	43.34
0.9189	43.22	42.81	42.69	42.58	42.49	42.47
1.1445	42.12	41.86	41.67	41.58	41.57	41.59

(vii) L-glutamine in aqueous K2SO4 solution

Concentration	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
0.1926	46.95	46.57	46.22	45.97	45.86
0.2320	46.62	46.21	45.83	45.71	45.52
0.2717	46.26	45.95	45.68	45.47	45.39

(viii) L-glutamine in aqu eous KNO• 3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	51.04	50.55	50.18	49.90	49.73
0.0381	50.56	50.26	50.00	49.74	49.55
0.0766	50.22	49.82	49.68	49.57	49.38

0.1152	49.89	49.58	49.37	49.24	49.13
0.1542	49.53	49.26	48.98	48.95	48.82
0.1934	49.30	48.83	48.65	48.52	48.53
0.2330	49.00	48.57	48.44	48.30	48.19
0.2728	48.54	48.12	47.98	47.82	47.71

(ix) L-glutamine in aqueous KCl solution

Concentration	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	47.46	47.14	46.91	46.68	46.53
0.0379	47.32	46.92	46.73	46.42	46.28
0.0760	47.04	46.60	46.43	46.09	46.04
0.1145	46.77	46.42	46.14	45.94	45.71
0.1534	46.51	46.20	45.96	45.71	45.51
0.1925	46.14	45.85	45.61	45.46	45.31
0.2320	45.87	45.52	45.35	45.25	45.06
0.2718	45.53	45.26	45.01	44.85	44.81

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Table 2.2: Isothermal compressibility (KT2X10 , m N") as functions of concentration and temperature

(i) L-isoleucine in aqueous K2SO4 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0284	51.30	50.42	49.73	48.94	48.45	47.98
0.0474	51.02	50.28	49.61	48.85	48.35	47.90
0.0665	50.98	50.11	49.43	48.74	48.27	47.84
0.0857	50.72	50.00	49.11	43.02	48.13	47.68
0.1049	50.68	49.84	49.22	48.64	48.27	47.77
0.1243	50.63	49.80	49.08	48.49	48.01	47.54
0.1437	50.43	49.61	48.94	48.30	47.76	47.33
0.1633	50.30	49.52	48.87	48.16	47.67	47.23

(ii) L-isoIeucine in aqueous KNO3 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	53.97	52.98	52.15	51.44	50.82	50.32
0.0285	53.93	52.89	52.06	51.36	50.78	50.28
0.0477	53.81	52.80	51.96	51.28	50.71	50.24
0.0669	53.59	52.68	51.88	51.22	50.65	50.19
0.0862	53.32	52.38	51.63	51.14	50.61	50.10
0.1056	53.17	52.20	51.49	50.98	50.36	49.92
0.1250	52.97	52.08	51.43	50.86	50.13	49.74
0.1446	52.83	52.00	51.37	50.65	50.03	49.62

0.1642	52.71	51.82	51.14	50.58	49.93	49.55

(iii) L-isoleucine in aqueous KCl solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	49.66	49.01	48.45	47.89	47.43
0.0284	49.52	48.92	48.42	47.83	47.37
0.0474	49.47	48.88	48.38	47.79	47.31
0.0665	49.40	48.78	48.31	47.69	47.26
0.0856	49.31	48.66	48.18	47.64	47.21
0.1049	49.05	48.43	47.97	47.58	47.13
0.1243	48.97	48.33	47.85	47.45	46.94
0.1437	48.78	48.27	47.70	47.20	46.79
0.1632	48.62	48.12	47.60	47.07	46.65

(iv) L-proIine in aqueous K2SO4 solution

Concentration	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

(v) L-proline in aqueous KNO3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	52.98	52.15	51.44	50.82	50.32
0.0958	52.33	51.84	51.16	50.59	50.08
0.1932	51.85	51.30	50.74	50.18	49.69
0.2923	51.32	50.74	50.09	49.60	49.10
0.3932	50.96	50.37	49.72	49.05	48.66
0.4958	50.37	49.68	49.16	48.64	47.66
0.6002	49.63	49.15	48.52	47.95	47.62
0.7065	49.19	48.72	48.01	47.51	47.16
0.8146	48.83	48.22	47.61	47.17	46.67
0.9248	48.13	47.50	46.99	46.59	46.19
1.0371	47.69	47.12	46.65	46.31	45.96

(vi) L-proline in aqueous KCI solution

Concentration	298.15	303.15	308.15	313.15	318.15	323.15

0.0000	50.37	49.66	49.01	48.45	47.89	47.43
0.0950	50.16	49.40	48.71	48.04	47.47	47.05
0.2900	49.20	48.36	47.64	47.08	46.61	46.16
0.4920	45.39	44.89	44.67	44.42	44.33	44.26
0.7015	44.22	43.92	43.60	43.45	43.38	43.34
0.9189	46.03	45.32	44.87	44.45	44.06	43.74
1.1445	44.99	44.42	43.92	43.53	43.21	42.93

(vii) L-glutamine in aqueous K2SO4 solution

Concentration	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

(viii) L-glutamine in aq ueous KNO3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	52.98	52.15	51.44	50.82	50.32
0.0381	52.53	51.88	51.27	50.68	50.16
0.0766	52.23	51.47	50.98	50.52	50.01
0.1152	51.91	51.26	50.70	50.22	49.78
0.1542	51.58	50.97	50.34	49.96	49.50
0.1934	51.37	50.57	50.04	49.58	49.24
0.2330	51.09	50.33	49.85	49.37	48.93
0.2728	50.66	49.92	49.43	48.93	48.50

(ix) L-glutamine in aqueous KCI solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	49.66	49.01	48.45	47.89	47.43
0.0379	49.53	48.80	48.28	47.66	47.20
0.0760	49.27	48.51	48.01	47.36	46.99
0.1145	49.02	48.35	47.74	47.22	46.69
0.1534	48.78	48.14	47.57	47.02	46.50
0.1925	48.43	47.81	47.25	46.78	46.33
0.2320	48.18	47.51	47.02	46.60	46.10

0.2718	47.87	47.27	46.70	46.23	45.87

incompressible hydrated aggregates as a result of increase in temperature. The Kyi versus solute concentration plots (Fig. 2.1-2.9) exhibit linear behaviour in all the cases. The KTI 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 (157), P,= (ax/KT,)-? [2.3] The coefficient of thermal expansion, aj used in evaluating the internal pressure has been calculated (Appendix: Table Al) from the density data by using the following equation (271): aT=l/p(ap/aT)p. [2.4] The computed values of P, are listed in Table 2.3. The plots of Pj against solute concentration show linear behaviour in all the cases except those of L-glutamine in aqueous KCl in which irregular behaviour is shown at higher concentrations (Figs. 2.10-2.18). An examination of Table 2.3 reveals that the internal pressure values increase with increase in concentration of amino acids in aqueous electrolyte systems. The variation uith increase in concentration may be attributed to the overall increase of cohesive forces in solutions. Internal pressure values also increase \\ilh increase in temperature. This may be probable due to a decrease in the repulsive forces among the components of the systems with increase in temperature.

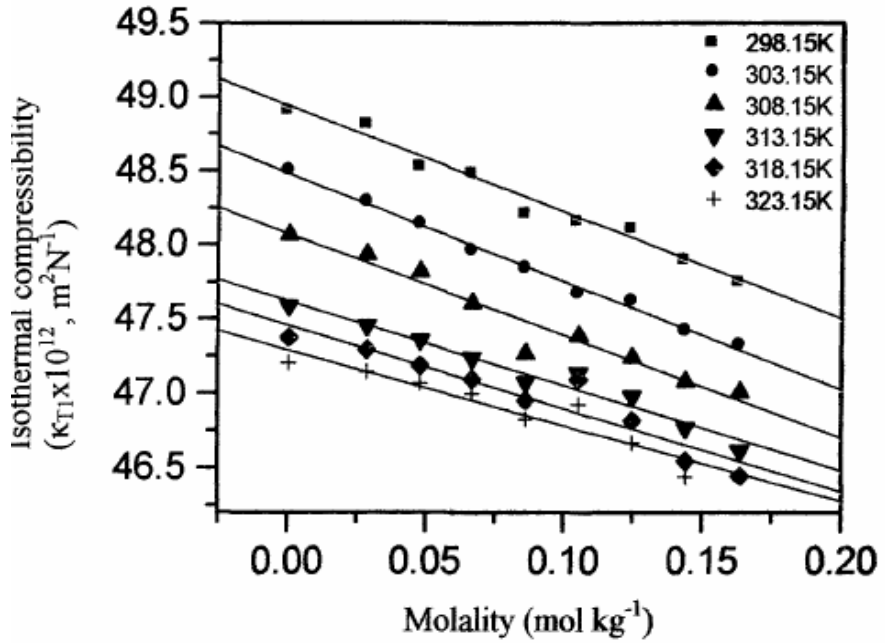


Fig.2.1: Plot of isothermal compressibility versus concentration of L-isoleucine in aqueous K_2S0_4 solution.

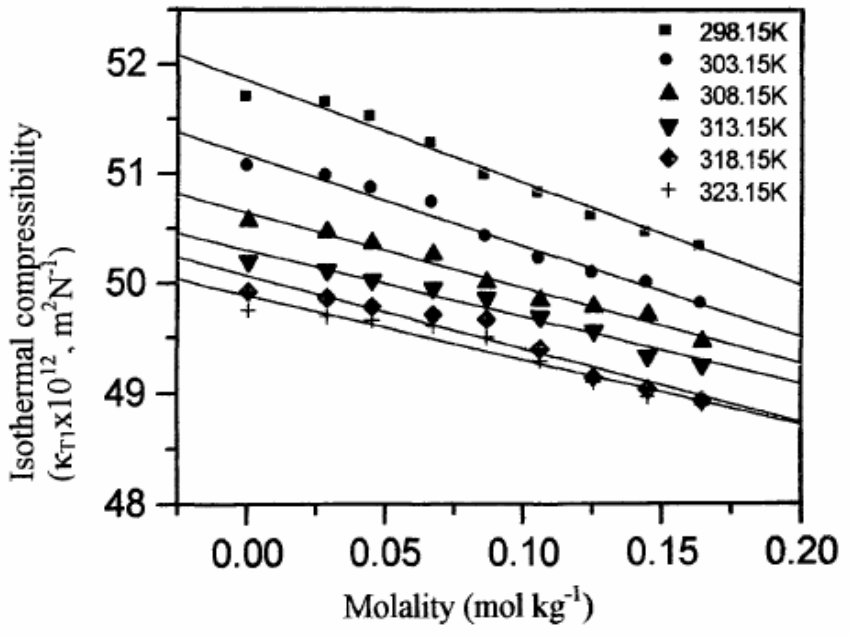


Fig.2.2: Plot of isothermal compressibility versus concentration of L-isoleucine in aqueous KNO_3 solution.

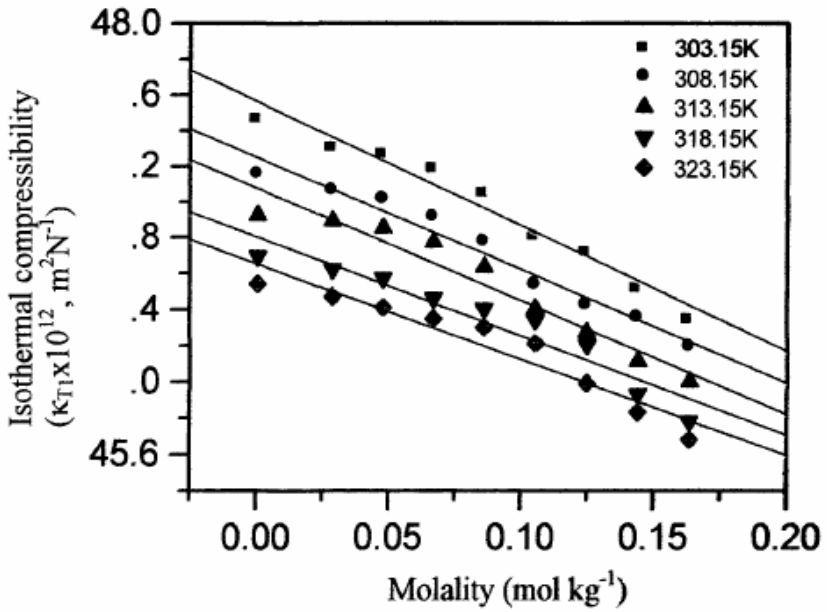


Fig.2.3: Plot of isothermal compressibility versus concentration of L-isoleucine in aqueous KCl solution.

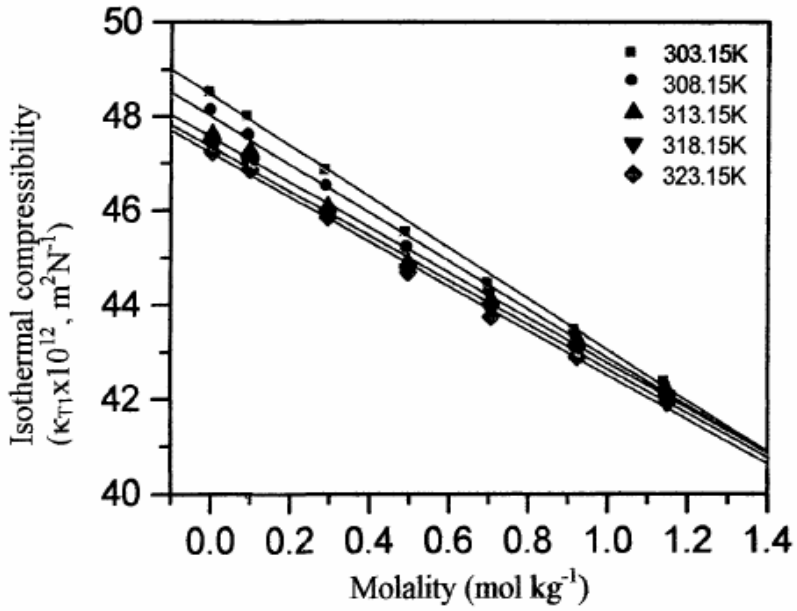


Fig.2.4: Plot of isothermal compressibility versus concentration of L-proline in aqueous K_2SO_4 solution.

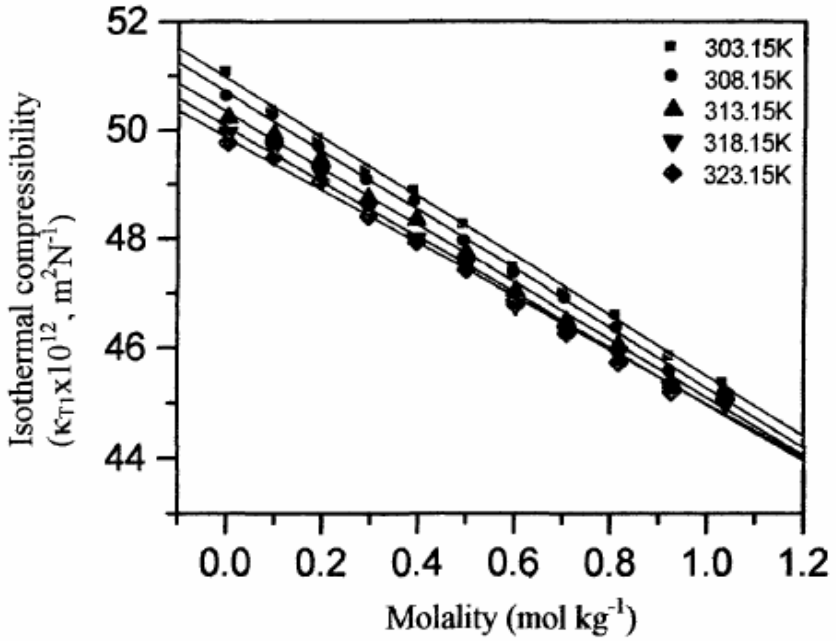


Fig.2.5: Plot of isothermal compressibility versus concentration of L-proline in aqueous KNO_3 solution.

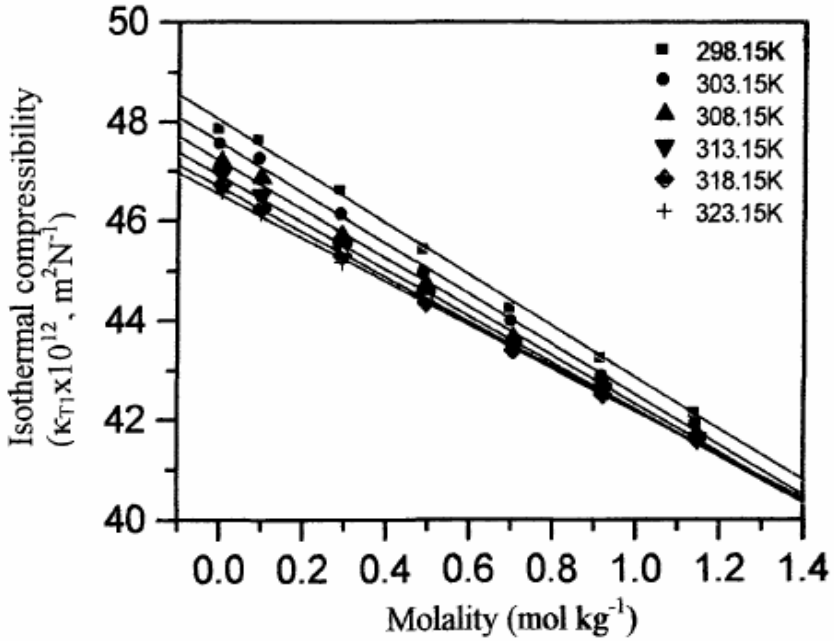


Fig.2.6: Plot of isothermal compressibility versus concentration of L-proline in aqueous KCl solution.

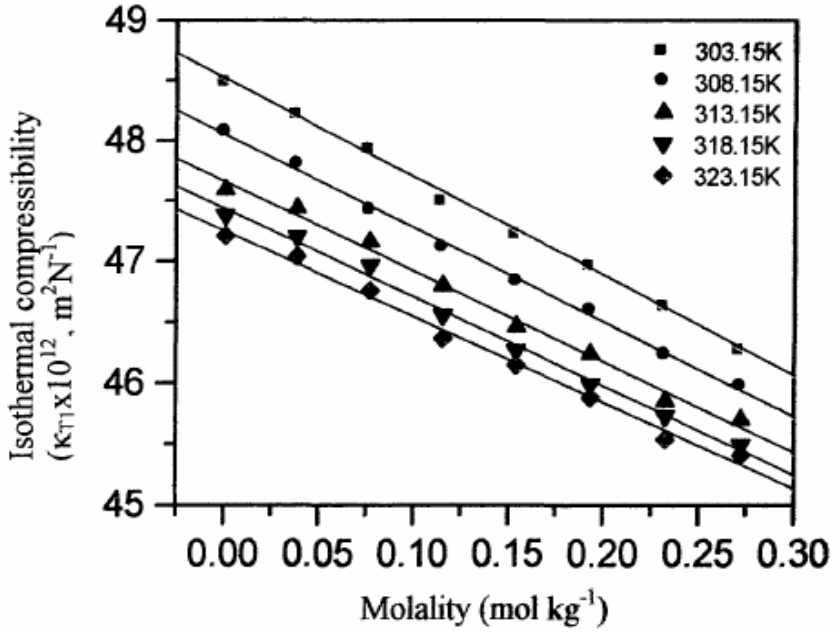


Fig.2.7: Plot of isothermal compressibility versus concentration of L-glutamine in aqueous K_2SO_4 solution.

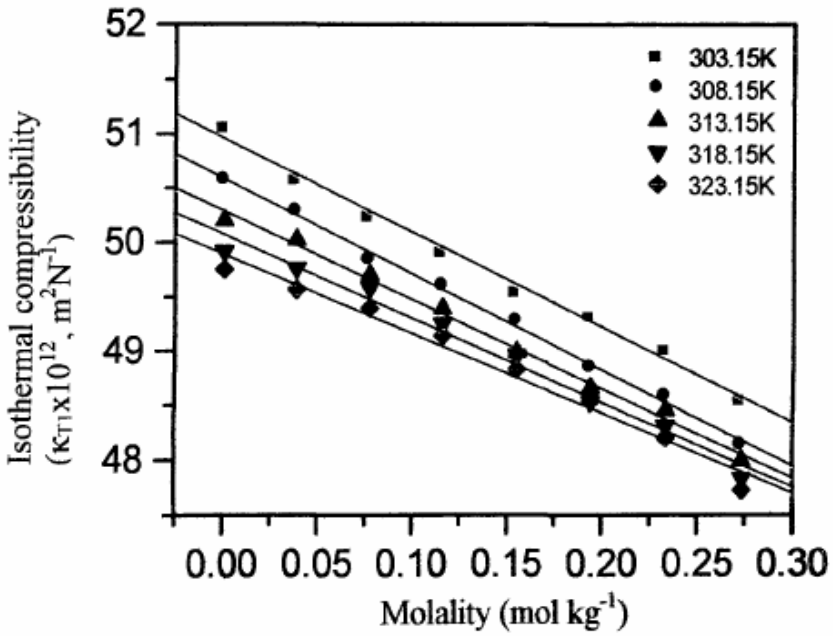


Fig.2.8: Plot of isothermal compressibility versus concentration of L-glutamine in aqueous KNO_3 solution.

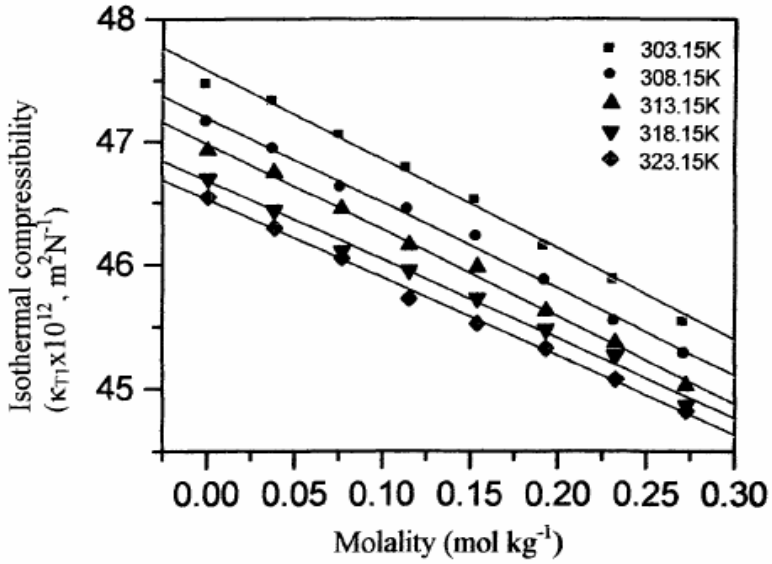


Fig.2.9: Plot of isothermal compressibility versus concentration of L-glutamine in aqueous KCl solution.

Table 2.3: Internal pressure (PjXlO", Nm") as functions of concentration and temperature

(i) L-isoleucine in aqueous K2SO4 solution

Concentration	298.15	303.15	308.15	313.15	318.15	323.15
0.0000	2.012	2.064	2.123	2.179	2.230	2.280
0.0284	2.072	2.134	2.188	2.249	2.297	2.346
0.0474	2.142	2.199	2.254	2.316	2.367	2.415
0.0665	2.201	2.266	2.324	2.385	2.435	2.484
0.0857	2.271	2.331	2.402	2.455	2.506	2.558
0.1049	2.331	2.399	2.457	2.515	2.562	2.618
0.1243	2.391	2.461	2.526	2.587	2.642	2.698
0.1437	2.459	2.531	2.596	2.661	2.722	2.777
0.1633	2.525	2.596	2.661	2.732	2.792	2.843

(ii) L-isoIeucine in aqueous KNO3 solution

Concentration	298.15	303.15	308.15	313.15	318.15	323.15
0.0000	2.244	2.310	2.377	2.440	2.499	2.554
0.0285	2.298	2.372	2.440	2.502	2.560	2.615
0.0477	2.303	2.377	2.444	2.506	2.564	2.617
0.0669	2.424	2.496	2.565	2.628	2.689	2.744
0.0862	2.437	2.511	2.578	2.633	2.691	2.749
0.1056	2.499	2.577	2.644	2.701	2.767	2.823
0.1250	2.509	2.583	2.647	2.708	2.781	2.834
0.1446	2.571	2.644	2.709	2.780	2.848	2.904
0.1642	2.633	2.711	2.781	2.845	2.916	2.972

(iii) L-isoleucine in aqueous KCI solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	2.287	2.347	2.397	2.454	2.507
0.0284	2.414	2.471	2.525	2.586	2.641
0.0474	2.476	2.535	2.590	2.653	2.710
0.0665	2.480	2.540	2.594	2.659	2.713
0.0856	2.547	2.610	2.665	2.727	2.780
0.1049	2.620	2.685	2.741	2.795	2.853
0.1243	2.625	2.690	2.749	2.803	2.866
0.1437	2.696	2.756	2.822	2.885	2.942
0.1632	2.767	2.829	2.892	2.959	3.019

(iv) L-proline in aqueous K2SO4 solution

Concentration	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

(v) L-proline in aqueous KNO3 solution

Concentration	303.15	313.15	318.15	323.15
0.0000	2.310	2.377	2.440	2.499
0.0958	2.283	2.330	2.389	2.444
0.1932	2.473	2.528	2.586	2.645
0.2923	2.553	2.612	2.677	2.735
0.3932	2.568	2.628	2.693	2.763
0.4958	2.654	2.723	2.783	2.846
0.6002	2.751	2.810	2.880	2.949
0.7065	2.832	2.892	2.970	3.037
0.8146	2.909	2.981	3.055	3.120
0.9248	2.949	3.025	3.092	3.155
1.0371	3.035	3.108	3.175	3.220

(vi) L-proline in aqii ieous KCl solution

Concentration	298.15	303.15	313.15	318.15	323.15
0.0000	2.232	2.287	2.347	2.397	2.454
0.0950	2.236	2.297	2.356	2.417	2.474
0.2900	2.335	2.404	2.469	2.527	2.581

0.4920	45.39	44.89	44.67	44.42	44.33
0.7015	44.22	43.92	43.60	43.45	43.38
0.9189	2.548	2.618	2.674	2.730	2.785
1.1445	2.603	2.667	2.728	2.783	2.834

(vii) L-glutamine in aqueous K2SO4 solution

Concentration	**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
0.2320	2.432	2.498	2.565	2.618	2.675
0.2717	2.508	2.571	2.633	2.693	2.746

(viii) L-glutamine in aqueous KNO3 solution

Concentration	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	2.310	2.377	2.440	2.499	2.554
0.0381	2.161	2.213	2.265	2.318	2.368
0.0766	2.228	2.286	2.335	2.382	2.434
0.1152	2.296	2.351	2.405	2.455	2.505
0.1542	2.307	2.362	2.419	2.465	2.516
0.1934	2.372	2.437	2.492	2.543	2.590
0.2330	2.440	2.505	2.558	2.612	2.667
0.2728	2.458	2.524	2.578	2.634	2.688

(ix) L-glutamine in aqueous KCI solution

Concentration	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	2.287	2.347	2.397	2.454	2.507
0.0379	2.172	2.230	2.279	2.335	2.384
0.0760	2.181	2.241	2.290	2.348	2.392
0.1145	2.191	2.247	2.301	2.352	2.406
0.1534	2.200	2.254	2.307	2.361	2.413
0.1925	2.214	2.268	2.321	2.370	2.420
0.2320	2.162	2.218	2.266	2.311	2.362
0.2718	2.175	2.227	2.280	2.329	2.372

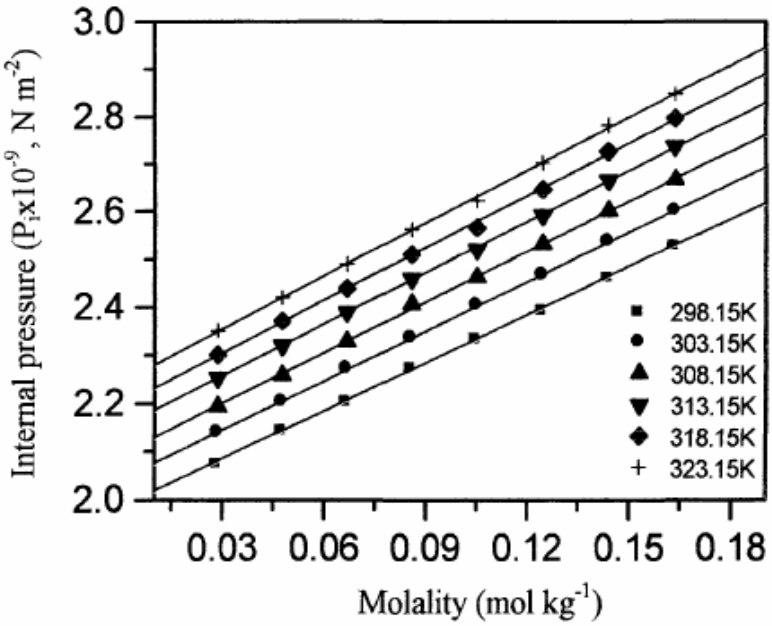


Fig.2.10: Plot of internal pressure versus concentration of L-isoleucine in aqueous K_2SO_4 solution.

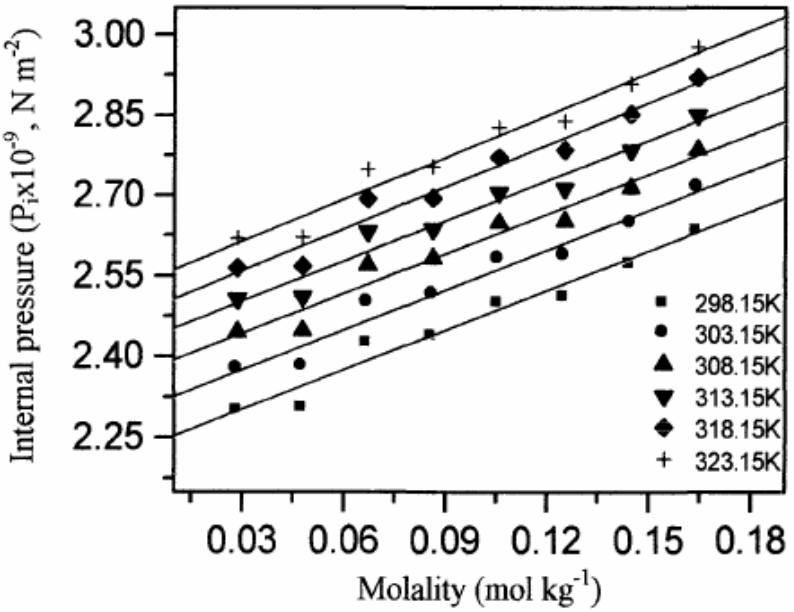


Fig.2.11: Plot of internal pressure versus concentration of L-isoleucine in aqueous KNO_3 solution.

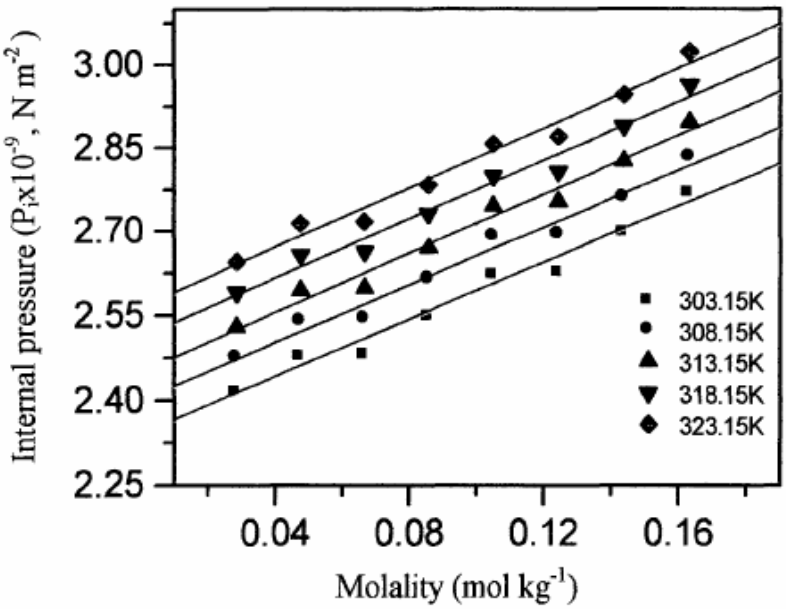


Fig.2.12: Plot of internal pressure versus concentration of L-isoleucine in aqueous KCl solution .

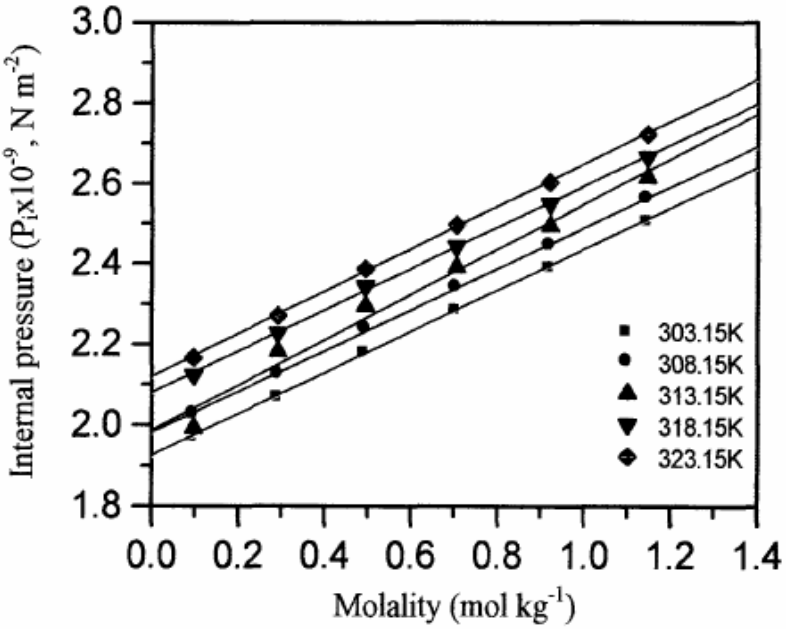


Fig.2.13: Plot of internal pressure versus concentration of L-proline in aqueous K_2SO_4 solution.

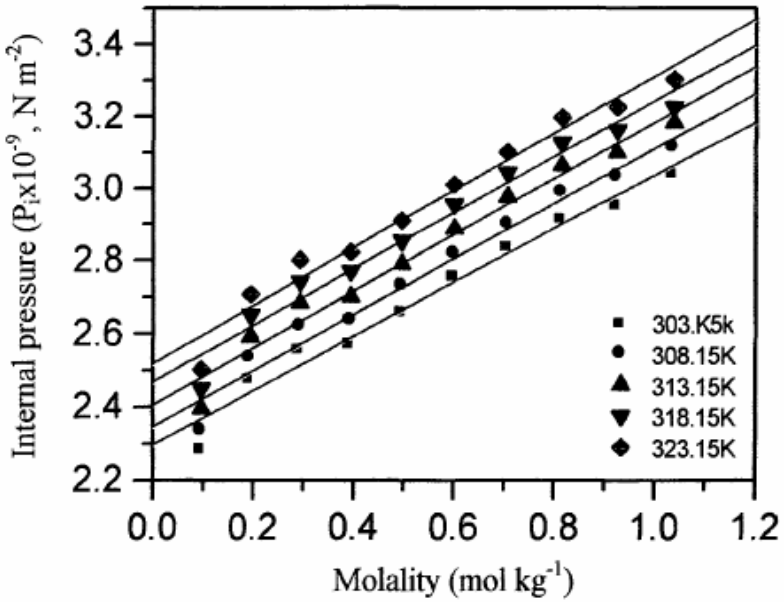


Fig.2.14: Plot of internal pressure versus concentration of L-proline in aqueous KNO_3 solution.

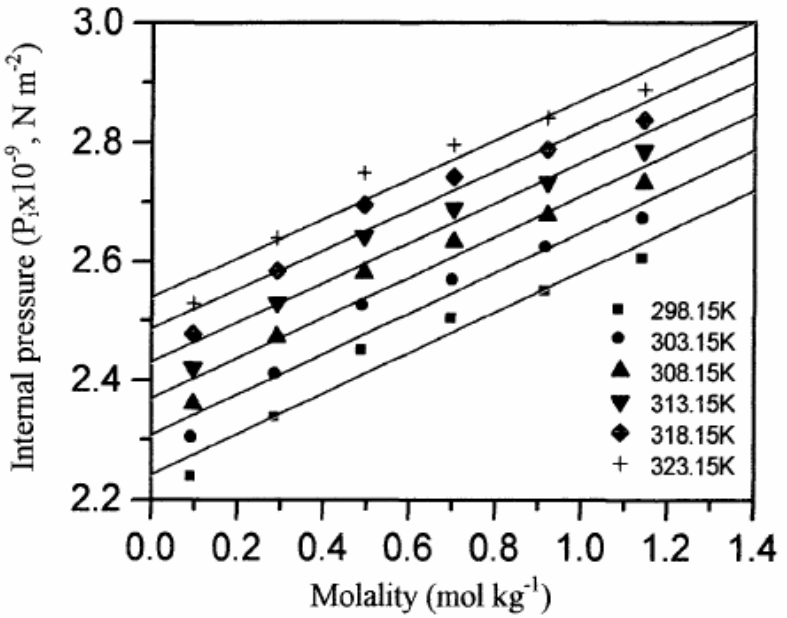


Fig.2.15: Plot of internal pressure versus concentration of L-proline in aqueous KCl solution.

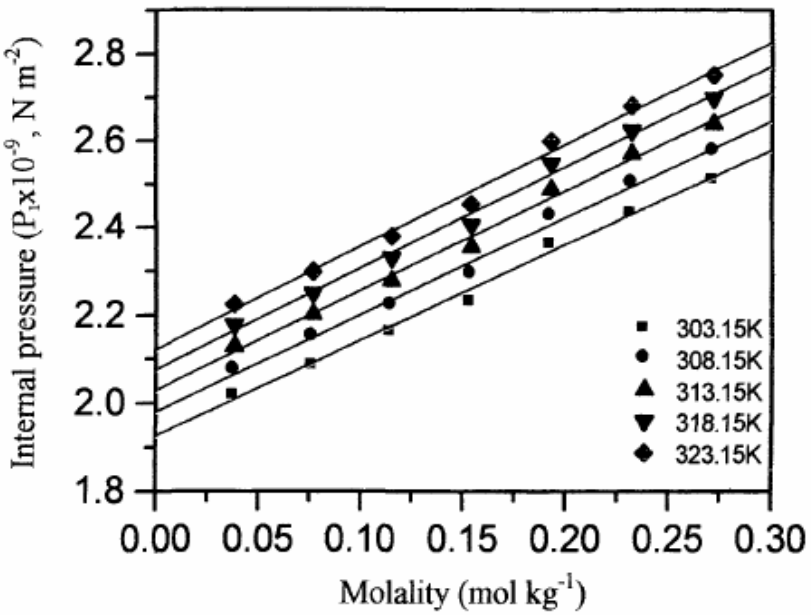


Fig.2.16: Plot of internal pressure versus concentration of L-glutamine in aqueous K_2SO_4 solution.

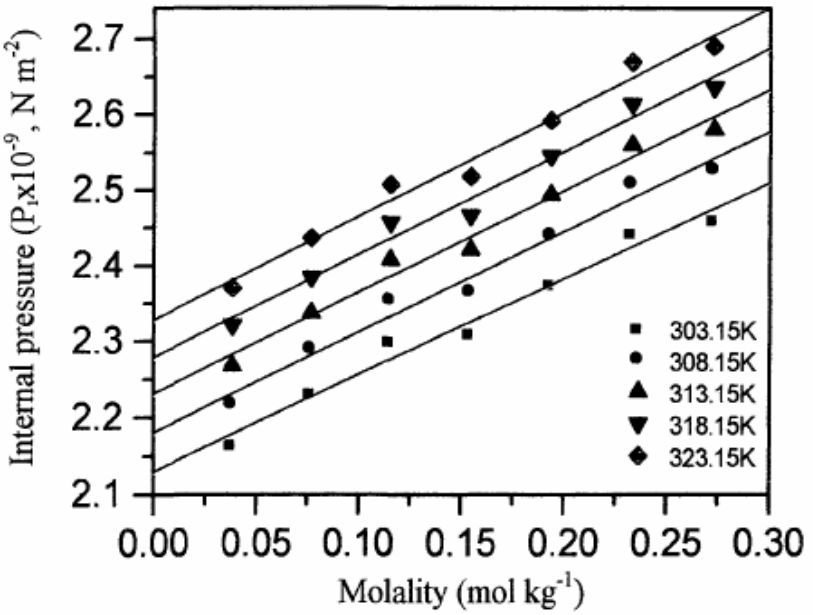


Fig.2.17: Plot of internal pressure versus concentration of L-glutamine in aqueous KNO_3 solution.

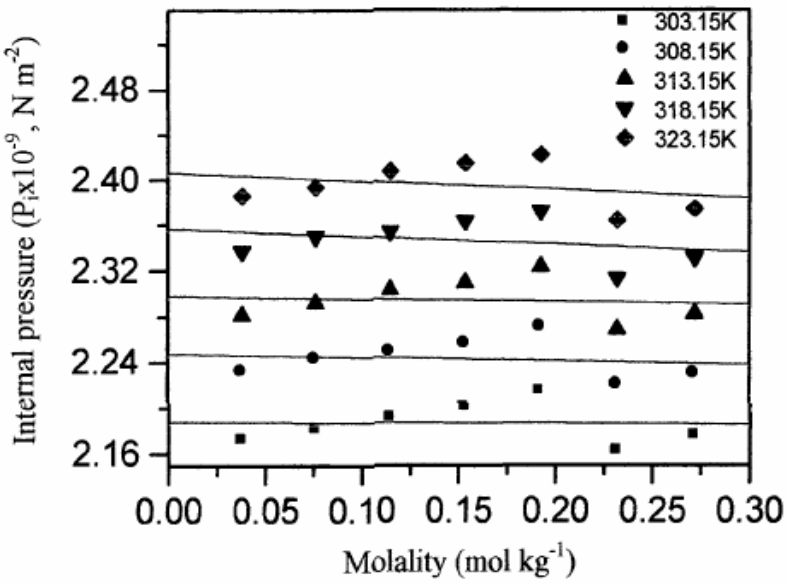


Fig.2.18: Plot of internal pressure versus concentration of L-glutamine in aqueous KCl solution.

The solubility parameter has been calculated by using the following equation (271), 5 = (ax/KT,)'^'. [2.5] The calculated values have been presented in Table 2.4. These values have been found to increase with increase in concentration of amino acids as well as with increase in temperature. The trend of variation of 5 with concentration and temperature is similar to that of internal pressure since it is the square root of P,. The Pseudo-Gruneisen parameter, F, which happens to be a measure of the degree of molecular / ionic association has been evaluated using the relation, r = y-l/aTT [2.6] in which ot^and T have their usual meaning. The specific heat ratio, y has been calculated using the equation, Y = Cp/Cv = KTI/KS. [2.7] The calculated values of y have been listed in Table A2 of appendix. The values of Pseudo-Gruneisen Parameter have been listed in Table 2.5. An examination of the table reveals that the values of F decrease with increase in temperature. This decrease may be due to an increase in the Icinetic energy of molecules, which in turn, increase the thermal motion of molecules and disrupts the molecular association. The F values also show a decreasing trend of variation with increase in amino acid concentration in aqueous electrolytic solutions. It may, however, be noted that such a variation with change in concentration of solute is insignificant.

Table 2.4: Solubility parameter, 5x10"'^, (Nm"^)''^ as functions of
concentration and temperature

(i) L-isoIeucine in aqueous K2SO4 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	4.486	4.543	4.608	4.668	4.722	4.775
0.0284	4.552	4.619	4.677	4.743	4.793	4.844
0.0474	4.628	4.689	4.747	4.813	4.865	4.915

0.0665	4.692	4.761	4.821	4.883	4.934	4.984
0.0857	4.766	4.829	4.901	4.955	5.006	5.058
0.1047	4.828	4.898	4.957	5.015	5.062	5.117
0.1243	4.890	4.960	5.026	5.086	5.140	5.194
0.1437	4.959	5.031	5.095	5.159	5.217	5.270
0.1633	5.025	5.095	5.159	5.227	5.284	5.332

(ii) L-isoleucine in aqueous KNO3 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	4.737	4.806	4.875	4.940	4.999	5.054
0.0285	4.794	4.871	4.939	5.002	5.060	5.114
0.0477	4.799	4.875	4.944	5.006	5.063	5.116
0.0669	4.923	4.996	5.064	5.123	5.186	5.239
0.0862	4.936	5.011	5.077	5.131	5.187	5.243
0.1056	4.999	5.076	5.142	5.197	5.260	5.313
0.1250	5.009	5.082	5.143	5.204	5.273	5.324
0.1446	5.071	5.142	5.205	5.273	5.337	5.389
0.1642	5.131	5.207	5.273	5.334	5.400	5.451

(iii) L-isoleucine in aqueous KCl solution

Concentration	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	4.782	4.845	4.896	4.954	5.007
0.0284	4.914	4.971	5.025	5.085	5.139
0.0474	4.976	5.035	5.089	5.151	5.206
0.0665	4.980	5.040	5.093	5.156	5.208
0.0856	5.046	5.108	5.162	5.222	5.275
0.1049	5.118	5.181	5.236	5.287	5.342
0.1243	5.123	5.187	5.243	5.294	5.353
0.1437	5.193	5.250	5.312	5.371	5.424
0.1632	5.260	5.319	5.378	5.439	5.494

(iv) L-proline in aqueous K2SO4 solution

Concentration	**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

(v) L-proline in aqueous KNO3 solution

Concentration	303.15	313.15	318.15	323.15
0.0000	4.806	4.875	4.940	4.999
0.0958	4.778	4.827	4.887	4.943
0.1932	4.973	5.028	5.085	5.142
0.2923	5.053	5.111	5.174	5.230
0.3932	5.067	5.126	5.189	5.256
0.4958	5.151	5.218	5.275	5.335
0.6002	5.245	5.301	5.367	5.431
0.7065	5.322	5.378	5.450	5.510
0.8146	5.394	5.460	5.527	5.585
0.9248	5.431	5.500	5.561	5.617
1.0371	5.509	5.575	5.635	5.675

(vi) L-proIine in aqiu eous KCI solution

Concentration	298.15	303.15	313.15	318.15	323.15
0.0000	4.724	4.782	4.845	4.896	4.954
0.0950	4.729	4.793	4.854	4.916	4.974
0.2900	4.832	4.903	4.969	5.027	5.081
0.4920	45.39	44.89	44.67	44.42	44.33
0.7015	44.22	43.92	43.60	43.45	43.38
0.9189	5.048	5.117	5.171	5.225	5.277
1.1445	5.102	5.164	5.223	5.275	5.324

(vii) L-glutamine in aqueous K2SO4 solution

Concentration	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

(viii) L-glutamine in aqu eous KNO> 3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	4.806	4.875	4.940	4.999	5.054
0.0381	4.648	4.704	4.759	4.814	4.867
0.0766	4.720	4.782	4.832	4.881	4.934

0.1152	4.791	4.849	4.904	4.955	5.005
0.1542	4.804	4.860	4.919	4.964	5.016
0.1934	4.870	4.937	4.992	5.043	5.089
0.2330	4.939	5.005	5.058	5.111	5.164
0.2728	4.957	5.024	5.077	5.132	5.185

(ix) L-glutamine in aqueous KCl solution

Concentration	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	4.782	4.845	4.896	4.954	5.007
0.0379	4.660	4.722	4.773	4.832	4.882
0.0760	4.670	4.734	4.785	4.846	4.891
0.1145	4.681	4.740	4.797	4.850	4.905
0.1534	4.690	4.748	4.803	4.859	4.913
0.1925	4.706	4.763	4.818	4.869	4.919
0.2320	4.650	4.709	4.760	4.808	4.860
0.2718	4.664	4.719	4.775	4.825	4.870

Table 2.5: Pseudo-Gruneisen parameter (F) as functions of concentration
and temperature

(i) L-isoleucine in aqueous K2SO4 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	-8.875	-8.729	-8.562	-8.426	-8.269	-8.115
0.0284	-8.632	-8.480	-8.330	-8.185	-8.040	-7.898
0.0474	-8.403	-8.254	-8.108	-7.964	-7.824	-7.686
0.0665	-8.185	-8.039	-7.896	-7.757	-7.619	-7.484
0.0857	-7.979	-7.835	-7.696	-7.560	-7.426	-7.294
0.1049	-7.782	-7.642	-7.505	-7.371	-7.240	-7.112
0.1243	-7.595	-7.458	-7.324	-7.193	-7.065	-6.940
0.1437	-7.418	-7.282	-7.151	-7.023	-6.898	-6.776
0.1633	-7.248	-7.116	-6.987	-6.862	-6.739	-6.619

(ii) L-isoleii icine in aqueous KNO3 solution

Concentration	**298.15**	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0000	-7.519	-7.396	-7.258	-7.124	-6.994	-6.869
0.0285	-7.348	-7.217	-7.087	-6.960	-6.835	-6.713
0.0477	-7.350	-7.219	-7.089	-6.962	-6.837	-6.714
0.0669	-7.020	-6.893	-6.769	-6.646	-6.527	-6.410
0.0862	-7.022	-6.896	-6.772	-6.649	-6.529	-6.411
0.1056	-6.869	-6.745	-6.622	-6.503	-6.385	-6.270

0.1250	-6.872	-6.747	-6.624	-6.504	-6.387	-6.272
0.1446	-6.726	-6.603	-6.482	-6.364	-6.250	-6.137
0.1642	-6.585	-6.465	-6.346	-6.230	-6.118	-6.008

(iii) L-isoleucine in aqueous KCl solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	-8.050	-7.898	-7.771	-7.627	-7.489
0.0284	-7.650	-7.513	-7.379	-7.248	-7.120
0.0474	-7.467	-7.332	-7.201	-7.073	-6.948
0.0665	-7.468	-7.335	-7.203	-7.075	-6.949
0.0856	-7.294	-7.161	-7.033	-6.907	-6.785
0.1049	-7.127	-6.997	-6.872	-6.748	-6.628
0.1243	-7.128	-6.999	-6.873	-6.749	-6.630
0.1437	-6.970	-6.842	-6.718	-6.598	-6.481
0.1632	-6.817	-6.691	-6.571	-6.453	-6.339

(iv) L-proline in aqueous K2SO4 solution

Concentration	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

(v) L-proline in aqueous KNO3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	-7.396	-7.258	-7.124	-6.994	-6.869
0.0958	-7.594	-7.457	-7.324	-7.193	-7.064
0.1932	-7.083	-6.956	-6.831	-6.708	-6.589
0.2923	-6.943	-6.818	-6.695	-6.574	-6.456
0.3932	-6.962	-6.836	-6.713	-6.593	-6.474
0.4958	-6.827	-6.703	-6.582	-6.463	-6.348
0.6002	-6.698	-6.576	-6.458	-6.341	-6.226
0.7065	-6.573	-6.453	-6.337	-6.223	-6.110
0.8146	-6.455	-6.336	-6.223	-6.109	-5.999
0.9248	-6.473	-6.354	-6.240	-6.126	-6.015
1.0371	-6.358	-6.241	-6.129	-5.956	-5.907

(vi) L-proIine in aqueous KCI solution

Concentration	298.15	303.15	308.15	313.15	318.15	323.15
0.0000	-8.185	-8.050	7.898	-7.771	-7.627	-7.489
0.0950	-8.208	-8.063	7.920	-7.780	-7.642	-7.506
0.2900	-8.037	-7.895	7.755	-7.618	-7.482	-7.349
0.4920	45.39	44.89	44.67	44.42	44.33	44.26
0.7015	44.22	43.92	43.60	43.45	43.38	43.34
0.9189	-7.954	-7.813	-7.673	-7.536	-7.401	-7.268
1.1445	-7.993	-7.850	-7.710	-7.572	-7.436	-7.302

(vii) L-glutamine in aqueous K2SO4 solution

Concentration	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
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

(viii) L-glutamine in aqueous KNO> 3 solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	-7.396	-7.258	-7.124	-6.994	-6.869
0.0381	-7.986	-7.846	-7.705	-7.568	-7.433
0.0766	-7.799	-7.662	-7.524	-7.389	-7.258
0.1152	-7.621	-7.486	-7.351	-7.220	-7.091
0.1542	-7.639	-7.503	-7.367	-7.236	-7.106
0.1934	-7.468	-7.336	-7.204	-7.075	-6.947
0.2330	-7.306	-7.117	-7.046	-6.922	-6.796
0.2728	-7.323	-7.193	-7.062	-6.936	-6.810

(ix) L-glutamine in aqiL ieous KCI solution

Concentration	303.15	308.15	313.15	318.15	323.15
0.0000	-8.050	-7.898	-7.771	-7.627	-7.489
0.0379	-8.503	-8.353	-8.205	-8.061	-7.920
0.0760	-8.517	-8.367	-8.219	-8.075	-7.933
0.1145	-8.530	-8.380	-8.233	-8.088	-7.946
0.1534	-8.544	-8.394	-8.246	-8.101	-7.959
0.1925	-8.557	-8.407	-8.260	-8.114	-7.973

0.2320	-8.816	-8.662	-8.510	-8.360	-8.214
0.2718	-8.830	-8.675	-8.524	-8.374	-8.228

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