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Partial Molal Volumes and Partial Molal Isentropic Compressibilities Of L-Isoleucine, L-Proline And L-Glutamine in Aqueous K2SO4, KNO3 and KCl Solutions

Riffat Basharat

Government Degree College Sumbal
Email: riffatbasharat5@gmail.com

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 K_2SO_4, 1 M KNO_3 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.

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

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,

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

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 studies of volumetric properties of solutes have proved to be of great importance in understanding the intermolecular / interionic interactions in solutions. The volumetric properties are known to be sensitive to the degree and nature of solute solvation (64,74,272,273).

The addition of salt / co-solvent to protein solution is known to affect their structure and configuration (121). Amino acids are essentially zwitterions in aqueous solutions (274-276). The volumetric and compressibility properties of amino acid reflect the solute-solute and solute-solvent interactions in solution. Amino acids and peptides on dissolving in aqueous medium cause a decrease in the volume of water. This is due to the contraction of water near the end groups and is termed as electrostriction (198).

Partial molal volume, a thermodynamic quantity provides important information about the solute-solvent interactions in solutions. The values for amino acids and peptides in aqueous electrolyte solutions exhibit the combined contributions of various hydrophilic and hydrophobic interactions. A number of studies have been made for the determination of partial molal volumes of amino acids in aqueous medium (32,34,41,42,45,47,48), aqueous electrolytes (60,92,105,106,108-110,113,115,117,194), and organic solvents (46,107,195-199).

Partial molal isentropic compressibility is also a thermodynamic property and is particularly a measure of hydration behaviour in aqueous solutions (10,277). The apparent molal volumes and apparent molal isentropic compressibilities at infinite dilution, which are also known as partial molal volumes and partial molal isentropic compressibilities, respectively, have been used to obtain information about the structural and interaction phenomena associated with the solvation process (278,279). These properties of a solute are known to be independent of the solute-solute interaction.

Consequently, with a view to understanding the solute-solvent intermolecular / interionic interactions, the partial molal volumes and partial molal isentropic compressibilities of amino acids: L-isoleucine, L-proline and L-glutamine in aqueous solutions of K2SO4, KNO3 and KCl have been determined as function of temperature.

RESULTS AND DISCUSSION

Apparent molal volumes (φ_v) of amino acids in aqueous electrolytic solutions have been evaluated from the density data using the relation,

$$\varphi_v = (M/\rho) - \{1000\ (\rho - \rho_o)/m\rho\rho_o\} \qquad [3.1]$$

where M, m ρ, ρ_o are the molar mass, molality, density of solution and that of the solvent, respectively. The apparent molal volume values have been listed in Table 3.1. The plots of φ_v with solute concentration exhibit apparently linear behaviour in L-isoleucine unlike those of L-proline and L-glutamine, which show non-linear behaviour (Figs. 3.1 - 3.9). The φ_v values have been least-squares fitted to the following equation,

$$\varphi_v = \varphi_v^o + S_v m \qquad [3.2]$$

where φ_v^o is the apparent molal volume at infinite dilution or partial molal volume and S_v is the slope of φ_v versus m plot. Few very far off data points particularly in the low concentration range have been ignored in fitting the data to the relevant equation. The φ_v^o and S_v values have been

Table 3.1: Apparent molal volume ($\varphi_v \times 10^6$, m^3 mol^{-1}) as functions of concentration and temperature

(i) L-isoleucine in aqueous K2SO4 solution

Concentration (mol kg^{-1})	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0284	107.96	111.22	114.55	114.69	118.06	118.31
0.0474	106.71	110.59	114.52	116.59	118.70	118.95
0.0665	107.51	110.32	114.53	116.05	118.97	120.59
0.0857	106.91	111.32	114.51	115.74	118.06	119.37
0.1049	106.53	110.93	114.54	116.41	119.21	119.46
0.1243	106.99	110.73	114.50	116.88	119.28	119.53
0.1437	106.70	111.22	115.14	116.58	118.69	119.58
0.1633	107.04	110.48	114.50	116.36	118.80	119.61

(ii) L-isoleucine in aqueous KNO3 solution

Concentration (mol kg^{-1})	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0285	105.44	108.72	112.07	115.46	115.67	115.94
0.0477	107.33	111.26	113.34	113.54	115.69	115.96
0.0669	106.79	109.63	112.52	115.46	115.71	117.32
0.0862	107.54	110.84	112.06	114.39	115.68	117.02
0.1056	107.16	109.88	113.51	114.58	116.56	117.70
0.1250	107.62	110.67	113.04	114.72	116.43	116.68
0.1446	107.33	109.99	113.33	114.81	115.68	116.58
0.1642	107.11	110.03	112.99	114.89	116.25	117.07

(iii) L-isoleucine in aqueous KCl solution

Concentration (mol kg^{-1})	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0284	107.75	111.02	114.33	117.68	117.91	118.15
0.0474	106.50	108.51	112.44	114.52	116.64	116.88
0.0665	107.31	110.12	111.63	114.51	116.09	116.33
0.0856	106.71	108.93	113.27	115.57	116.85	117.09
0.1049	107.18	109.02	112.61	114.53	116.46	116.70

0.1243	106.79	109.81	112.87	115.24	116.20	116.43
0.1437	106.50	109.14	112.43	115.14	115.99	116.23
0.1632	106.84	109.73	113.21	114.51	115.85	116.08

(iv) L-proline in aqueous K2SO4 solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0953	98.18	96.41	96.52	94.77	94.92	95.09
0.2909	88.75	88.23	88.63	88.44	88.88	88.71
0.4934	86.89	86.78	87.06	86.98	87.48	87.62
0.7032	86.08	86.16	86.38	86.49	86.87	87.02
0.9206	85.63	85.71	86.00	86.22	86.53	86.68
1.1462	85.35	85.51	85.76	86.04	86.32	86.55

(v) L-proline in aqueous KNO3 solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0958	83.62	85.60	86.66	86.79	86.93	87.08
0.1932	83.63	85.13	85.71	86.31	86.44	86.11
0.2923	83.13	84.34	85.07	85.51	85.96	86.43
0.3932	83.39	84.41	84.99	85.35	85.72	86.11
0.4958	83.25	84.27	84.94	85.25	85.76	85.91
0.6002	83.32	84.19	84.75	85.03	85.63	86.10
0.7065	83.23	84.24	84.88	85.14	85.54	85.96
0.8146	83.28	84.06	84.75	84.98	85.59	85.97
0.9248	83.22	84.12	84.85	84.86	85.52	85.88
1.0371	83.26	84.18	84.74	84.96	85.56	85.90

(vi) L-proline in aqueous KCl solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0950	94.20	93.38	92.56	92.69	92.85	93.98
0.2900	88.87	88.66	88.77	88.89	89.35	89.82
0.4920	87.81	87.72	88.01	88.32	88.46	88.99
0.7015	87.35	87.44	87.68	87.94	88.21	88.63

0.9189	87.20	87.19	87.40	87.73	87.97	88.43
1.1445	87.02	87.11	87.30	87.59	87.90	88.30

(vii) L-glutamine in aqueous K2SO4 solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0379	109.53	112.01	112.12	109.90	110.04	107.83
0.0762	101.28	103.75	105.02	103.96	105.27	104.24
0.1147	98.54	100.99	101.86	101.98	102.89	102.24
0.1535	97.15	99.03	100.28	100.98	101.69	101.83
0.1926	96.35	98.32	99.81	100.38	101.44	101.58
0.2320	95.40	97.85	99.09	99.98	100.88	101.02
0.2717	95.07	97.17	98.92	99.69	100.48	100.95

(viii) L-glutamine in aqueous KNO3 solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0381	105.42	100.82	93.79	93.89	91.59	89.29
0.0766	95.94	93.69	91.40	91.48	91.59	90.49
0.1152	92.78	92.11	90.61	91.49	90.79	90.89
0.1542	91.80	90.73	90.21	90.88	90.38	91.08
0.1934	90.73	90.37	89.97	90.53	90.14	91.20
0.2330	90.06	90.13	89.42	90.68	89.98	91.27
0.2728	89.51	89.62	89.36	90.45	90.20	91.32

(ix) L-glutamine in aqueous KCl solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0379	121.04	121.21	119.01	116.83	112.27	110.07
0.0760	110.46	110.61	109.56	108.53	106.32	105.29
0.1145	106.93	107.86	107.20	105.76	104.34	103.70
0.1534	105.17	106.49	105.43	104.97	103.94	102.90
0.1925	104.59	105.66	104.84	104.03	103.23	102.43
0.2320	103.80	105.11	104.06	103.40	102.76	102.11
0.2718	103.25	104.72	103.83	102.95	102.42	101.89

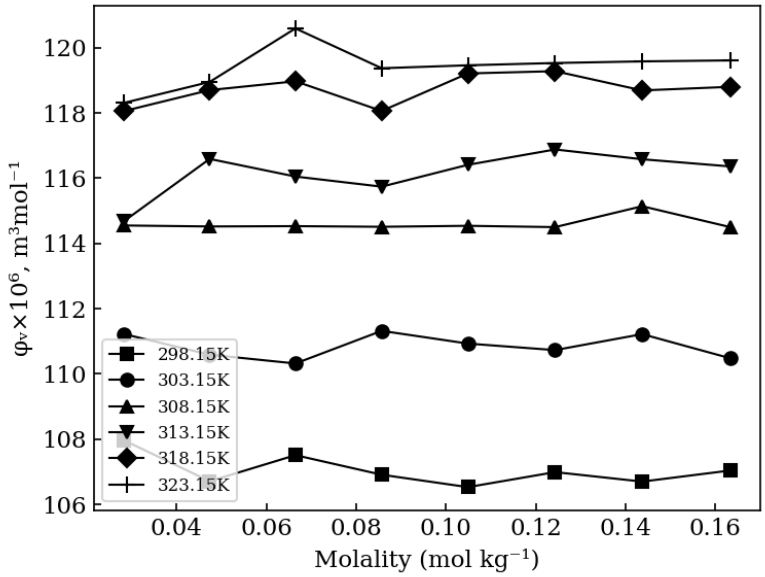


Fig.3.1: Plot of apparent molal volume versus concentration of L-isoleucine in aqueous K2SO4 solution.

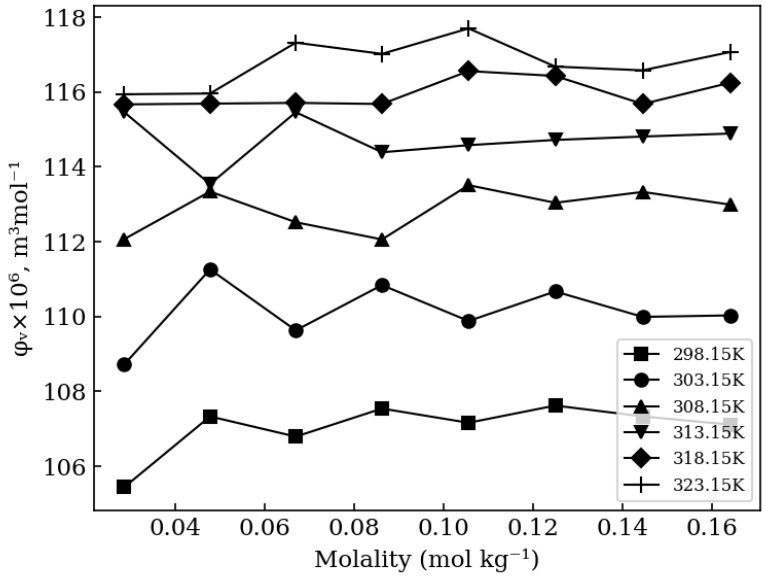


Fig.3.2: Plot of apparent molal volume versus concentration of L-isoleucine in aqueous KNO3 solution.

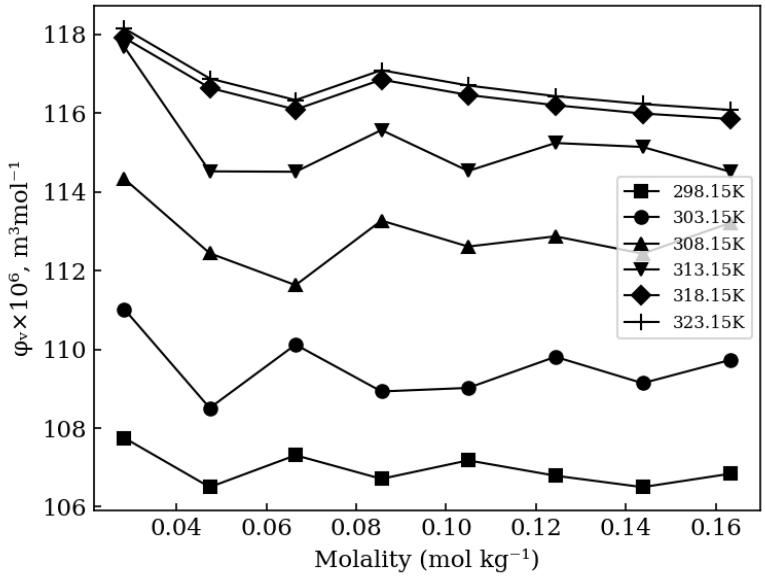


Fig.3.3: Plot of apparent molal volume versus concentration of L-isoleucine in aqueous KCl solution.

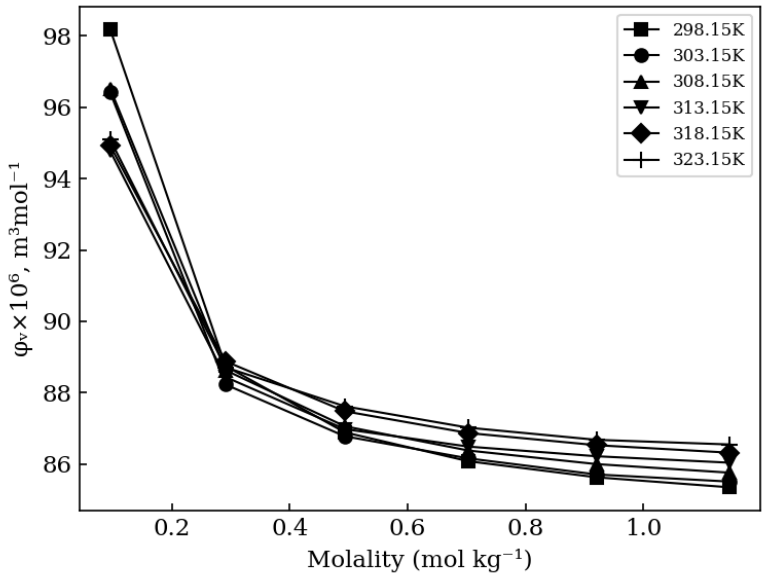


Fig.3.4: Plot of apparent molal volume versus concentration of L-proline in aqueous K2SO4 solution.

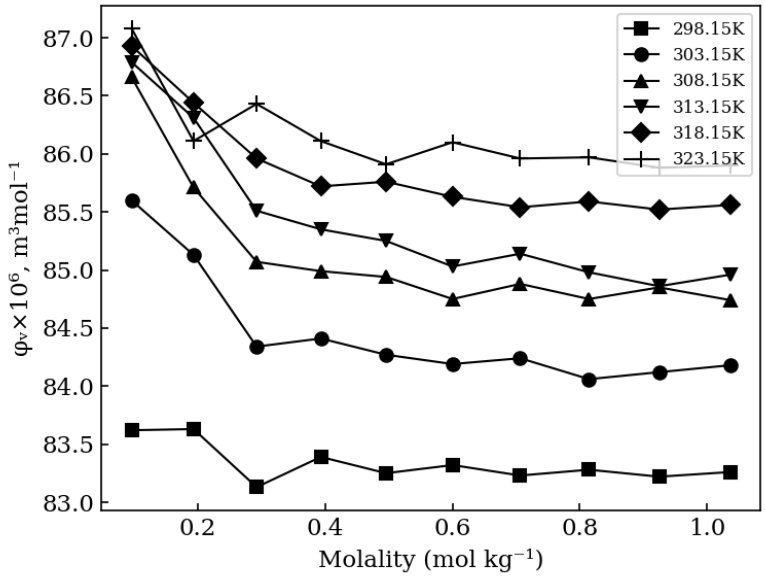


Fig.3.5: Plot of apparent molal volume versus concentration of L-proline in aqueous KNO3 solution.

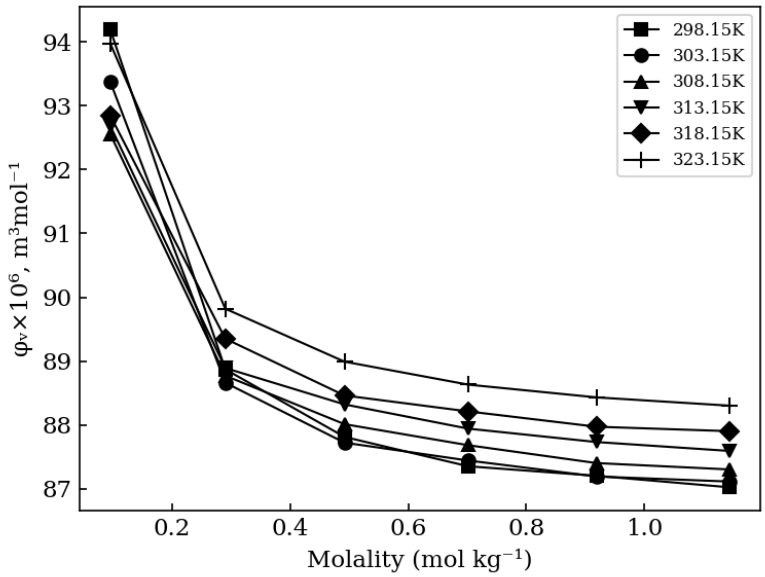


Fig.3.6: Plot of apparent molal volume versus concentration of L-proline in aqueous KCl solution.

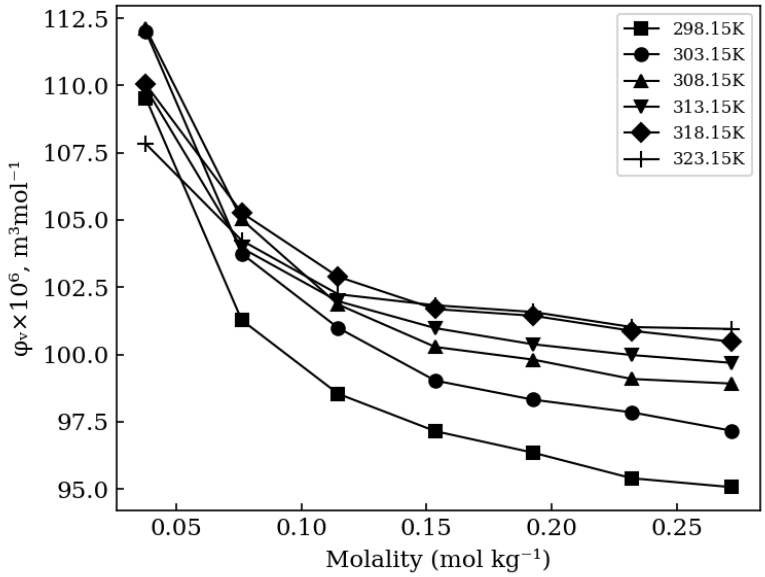


Fig.3.7: Plot of apparent molal volume versus concentration of L-glutamine in aqueous K2SO4 solution.

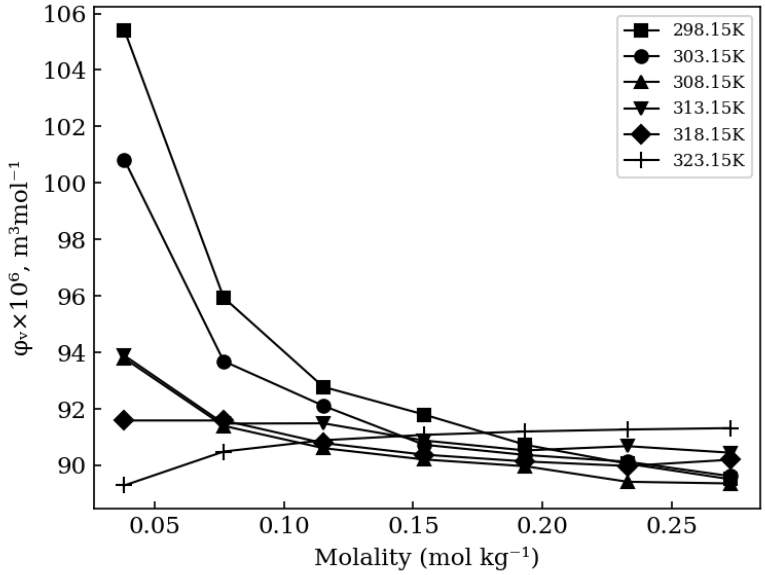


Fig.3.8: Plot of apparent molal volume versus concentration of L-glutamine in aqueous KNO3 solution.

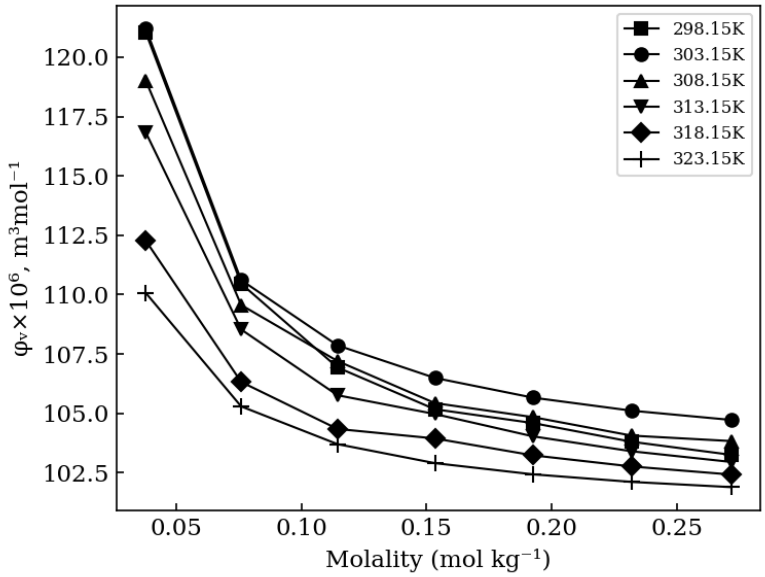


Fig.3.9: Plot of apparent molal volume versus concentration of L-glutamine in aqueous KCl solution.

given in Table 3.2. An examination of the table reveals that the partial molal volume values of the said amino acids, viz., L-isoleucine, L-proline and L-glutamine in aqueous electrolyte solutions at each temperature are higher than the corresponding values in aqueous medium. The positive values of φ_v^0 indicate relatively stronger solute-solvent interactions. The partial molal volume values for L-isoleucine and L-proline have been found to increase with increase in temperature from 298.15 to 323.15 K in all three aqueous electrolyte systems. The values for L-glutamine in K2SO4 solution increase between 298.15 and 308.15 K and after that the values decrease whereas in aqueous KNO3 solution the values increase between 298.15 and 303.15 K and then decrease upto 323.15 K. In aqueous KCl solution the φ_v^0 values of L-glutamine decrease from 298.15 to 323.15 K. The increase in φ_v^0 values for L-isoleucine and L-proline with temperature may be attributed to volume expansion of hydrated zwitterions of amino acids. The decrease in φ_v^0 values for L-glutamine in all the three solvents has been found to be significantly small. It is noteworthy that the φ_v^0 values in L-isoleucine-aqueous K2SO4, KNO3, and KCl solutions have been found to be 107.54, 106.31, and 107.39, respectively at 298.15 K while in aqueous medium it is found to be 105.80 cm^3/mol (72). These values in the said three electrolytes have been found to be 89.20, 83.52, and 89.07 cm^3/mol (82.83 cm^3/mol in aqueous medium) (64), respectively, in the case of L-proline while they are 102.52, 97.04, and 111.51 cm^3/mol (93.90 cm^3/mol in aqueous medium) (43), respectively, in that of L-glutamine at 298.15 K. These values are in accordance with those reported earlier. The partial molal volume of amino acids can be considered to be a sum of the geometric volume of solute and changes in the solvent due to its interaction with the

Table 3.2: The least-squares fit parameters of equation, $\varphi_v = \varphi_v^0 + S_v m$ at different temperatures

(i) L-isoleucine in aqueous K2SO4 solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	107.54	-5.185	0.40
303.15	110.90	-0.675	0.40
308.15	114.40	1.891	0.20
313.15	115.29	9.117	0.60
318.15	118.30	4.437	0.50
323.15	118.90	5.383	0.60

(ii) L-isoleucine in aqueous KNO3 solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	106.31	7.215	0.70
303.15	109.84	2.990	0.80
308.15	112.30	5.769	0.50
313.15	114.70	0.308	0.70
318.15	115.55	4.264	0.40
323.15	116.19	6.146	0.60

(iii) L-isoleucine in aqueous KCl solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	107.39	-4.601	0.40
303.15	109.93	-4.113	0.80
308.15	113.13	-2.947	0.80
313.15	116.26	-11.028	1.00
318.15	117.54	-10.945	0.50
323.15	117.79	-11.007	0.50

(iv) L-proline in aqueous K2SO4 solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	89.20	-3.739	0.60
303.15	88.63	-3.021	0.50
308.15	89.01	-3.155	0.50
313.15	88.67	-2.576	0.50
318.15	89.22	-2.816	0.50
323.15	89.05	-2.441	0.40

(v) L-proline in aqueous KNO3 solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	83.52	-0.329	0.10
303.15	85.15	-1.248	0.30
308.15	85.94	-1.453	0.40
313.15	86.38	-1.726	0.40
318.15	86.54	-1.218	0.30
323.15	86.62	-0.847	0.30

(vi) L-proline in aqueous KCl solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	89.07	-1.999	0.40
303.15	88.82	-1.684	0.30
308.15	89.00	-1.650	0.20
313.15	89.15	-1.484	0.20
318.15	89.49	-1.572	0.30
323.15	90.02	-1.671	0.30

(vii) L-glutamine in aqueous K2SO4 solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	102.52	-30.105	0.80
303.15	104.96	-31.381	1.00
308.15	105.80	-28.633	1.10
313.15	104.70	-20.383	0.60
318.15	105.93	-22.043	0.80
323.15	104.55	-14.843	0.60

(viii) L-glutamine in aqueous KNO3 solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	97.04	-30.070	0.90
303.15	94.48	-19.364	0.60
308.15	91.94	-10.188	0.20
313.15	91.93	-5.802	0.20
318.15	91.73	-6.981	0.30
323.15	90.36	3.930	0.10

(ix) L-glutamine in aqueous KCl solution

Temperature (K)	$\varphi_v^0 \times 10^6$ ($m^3\ mol^{-1}$)	$S_v \times 10^6$ ($m^3\ mol^{-2}\ kg$)	$\sigma \times 10^6$ ($m^3\ mol^{-1}$)
298.15	111.51	-33.502	1.10
303.15	111.60	-28.051	0.90
308.15	110.70	-28.148	0.80
313.15	109.47	-26.158	0.80
318.15	106.99	-18.171	0.50
323.15	105.86	-16.191	0.50

solute. The value may also be considered to be made up of van der Waals volume (Vvw), the volume associated with voids (Vv) or empty space, and the volume due to shrinkage (Vs) that is the result of electrostriction of the solvent caused by the hydrophilic groups present in the amino acids (115):

$$\varphi_v^0 = Vvw + Vv - Vs \qquad [3.3]$$

The slope, Sv is a measure of solute-solute interactions. The values have been found to be negative for all the systems under investigation except that of L-isoleucine in aqueous KNO3 and K2SO4 solutions for which the values are positive. The trend of variation of Sv with temperature for all three solutes seems irregular. The positive values of Sv indicate the stronger zwitterion-zwitterion and ion-ion interactions than those of apolar-apolar interactions. The negative Sv values, however, show that these interactions are weak and substantiate the view that unstable complex formation between the moieties takes place in these systems. The values of Sv are higher in the case of L-glutamine as compared to L-isoleucine and L-proline in all the aqueous electrolyte systems. The higher Sv values may be attributed to the presence of hydrophilic amide group in L-glutamine.

Apparent molal isentropic compressibility values of amino acids in aqueous electrolyte solutions have been determined using the relation,

$$\varphi k = [\{1000\ (\kappa s - \kappa_0)\}/m\rho_0] + \kappa_0\varphi v \qquad [3.4]$$

where m is the molality, ρ_0 is the density of solvent; and κs and κ_0 are the isentropic compressibilities of solution and solvent, respectively. The values of φk have been least-squares fitted to the equation,

$$\varphi k = \varphi k^0 + Skm \qquad [3.5]$$

where φk^0 is the apparent molal isentropic compressibility at infinite dilution or partial molal isentropic compressibility and is a measure of solute-solvent interactions. The Sk is the experimental slope representing the solute-solute interactions.

The values of φk have been listed in Table 3.3 while those of φk^0 and Sk values are given in Table 3.4. In all the examined systems the φk values show an irregular trend of variation with concentration (Figs. 3.10-3.18), but the values show increasing trend with temperature. This increasing trend with temperature may be attributed to a decrease in solute-solvent interactions. The trend of variation of φk^0 values with concentration for L-proline and L-glutamine is irregular while the values show an increasing trend for L-isoleucine in all the three solvent systems. The φk^0 values are either positive or negative of smaller magnitude in all the systems studied here. These values apparently indicate a larger ordering effect of the solute molecules on those of the solvent. The values of Sk are found to be negative, which suggest the presence of essentially weak solute-solute interactions in all the three amino acids.

Table 3.3: Apparent molal isentropic compressibility ($\varphi k \times 10^{11}$, $bar^{-1}m^3mol^{-1}$) as functions of concentration and temperature

(i) L-isoleucine in aqueous K2SO4 solution

Concentration (mol kg^{-1})	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0284	22.44	-4.41	14.19	14.21	26.04	32.29
0.0474	-10.53	-5.46	9.10	16.29	17.73	25.26
0.0665	0.21	-9.98	-1.21	9.44	16.89	24.62
0.0857	-11.89	-7.38	-17.89	4.63	11.48	15.43
0.1049	-4.87	-8.95	-1.07	15.88	27.21	27.20
0.1243	-0.05	-3.16	-0.24	11.40	14.52	16.00
0.1437	-4.29	-6.48	-1.54	5.81	5.45	9.09
0.1633	-4.52	-4.61	0.70	4.32	6.33	13.06

(ii) L-isoleucine in aqueous KNO3 solution

Concentration (mol kg^{-1})	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0285	22.66	23.28	22.27	28.10	34.74	34.69
0.0477	21.75	18.43	17.85	21.88	29.38	33.36
0.0669	4.56	12.73	16.35	22.82	27.09	32.43
0.0862	-8.66	-4.10	2.02	20.56	28.05	27.76
0.1056	-9.18	-7.71	0.77	14.34	14.37	18.25
0.1250	-12.10	-6.28	4.20	12.37	5.19	11.34
0.1446	-11.28	-3.51	6.54	6.30	5.58	10.09
0.1642	-10.03	-5.70	0.83	7.53	6.17	11.31

(iii) L-isoleucine in aqueous KCl solution

Concentration (mol kg^{-1})	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0284	6.54	21.92	38.23	28.85	28.83
0.0474	14.29	22.71	33.39	27.30	25.44
0.0665	14.71	18.38	28.34	21.36	25.31
0.0856	10.27	13.41	21.17	21.93	25.00
0.1049	0.89	3.41	10.33	21.66	22.51

0.1243	2.41	3.69	8.21	17.25	14.23
0.1437	-1.85	5.50	5.59	7.96	10.44
0.1632	-3.51	3.38	5.36	6.26	7.93

(iv) L-proline in aqueous K2SO4 solution

Concentration (mol kg⁻¹)	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0953	3.18	1.38	7.61	8.58	11.40
0.2909	-2.57	-1.59	-0.47	1.03	2.05
0.4934	-5.90	-5.25	-3.26	-2.39	-0.76
0.7032	-4.94	-3.32	-0.45	0.03	-0.18
0.9206	-3.99	-2.01	0.64	0.64	-0.81
1.1462	-3.94	-2.34	-0.22	0.46	0.56

(v) L-proline in aqueous KNO3 solution

Concentration (mol kg⁻¹)	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0958	-4.69	14.06	16.02	18.96	17.94
0.1932	-5.70	4.58	10.20	12.17	11.78
0.2923	-4.90	1.68	2.29	5.17	4.77
0.3932	-1.30	2.84	3.79	2.31	4.19
0.4958	-2.57	-0.86	1.65	2.74	3.28
0.6002	-5.39	-1.41	-0.90	-0.64	1.34
0.7065	-4.07	-0.59	-1.08	-0.16	1.12
0.8146	-2.52	-0.81	-0.30	1.01	0.08
0.9248	-4.00	-2.81	-1.58	-0.04	0.04
1.0371	-3.29	-1.74	-0.43	1.39	2.27

(vi) L-proline in aqueous KCl solution

Concentration (mol kg⁻¹)	Temperature (K)					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
0.0950	21.69	17.11	13.55	0.52	3.41	6.89
0.2900	6.82	2.94	0.57	0.32	2.10	2.36
0.4920	1.44	-0.94	0.34	-0.18	1.80	2.80
0.7015	-0.79	-0.45	-0.78	-0.01	0.15	2.55

0.9189	-0.76	-1.40	-0.08	0.72	1.77	2.75
1.1445	-1.40	-1.01	-0.43	0.41	1.72	2.77

(vii) L-glutamine in aqueous K2SO4 solution

Concentration (mol kg⁻¹)	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0379	-1.03	-0.89	18.75	11.65	14.54
0.0762	-4.78	-13.23	4.93	5.82	3.77
0.1147	-14.67	-13.05	-3.48	-5.94	-4.78
0.1535	-12.80	-11.71	-7.57	-6.49	-4.15
0.1926	-11.27	-9.57	-5.40	-6.88	-4.56
0.2320	-12.16	-11.67	-9.16	-6.62	-6.95
0.2717	-13.65	-10.57	-5.66	-5.76	-3.22

(viii) L-glutamine in aqueous KNO3 solution

Concentration (mol kg⁻¹)	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0381	-39.25	-8.77	11.50	14.55	10.08
0.0766	-27.95	-21.86	-1.64	13.33	11.06
0.1152	-24.29	-14.33	-5.28	3.21	6.46
0.1542	-23.45	-14.27	-10.59	0.09	1.74
0.1934	-18.51	-18.12	-11.70	-6.62	-0.54
0.2330	-17.25	-15.98	-8.83	-5.33	-3.63
0.2728	-20.45	-19.03	-13.26	-10.68	-9.22

(ix) L-glutamine in aqueous KCl solution

Concentration (mol kg⁻¹)	Temperature (K)				
	303.15	**308.15**	**313.15**	**318.15**	**323.15**
0.0379	22.76	6.91	14.51	-2.83	0.07
0.0760	7.82	-3.48	1.50	-8.20	0.11
0.1145	3.52	1.45	-1.95	-0.77	-5.85
0.1534	2.01	1.78	0.82	-0.01	-3.10
0.1925	-2.98	-2.66	-3.28	-0.74	-0.96
0.2320	-3.18	-4.69	-3.31	0.29	-1.38
0.2718	-5.23	-4.56	-5.72	-4.03	-1.64

Table 3.4: The least-squares fit parameters of equation, $\varphi k = \varphi k^0 + Skm$ at different temperatures

(i) L-isoleucine in aqueous K2SO4 solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
298.15	7.19	-9.290	1.10
303.15	-7.05	0.780	0.30
308.15	7.75	-7.850	0.90
313.15	16.42	-6.460	0.40
318.15	26.98	-11.800	0.60
323.15	33.91	-14.180	0.50

(ii) L-isoleucine in aqueous KNO3 solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
298.15	25.90	-27.250	0.80
303.15	25.37	-22.880	0.70
308.15	23.25	-14.980	0.50
313.15	32.05	-15.940	0.20
318.15	42.33	-24.460	0.40
323.15	43.22	-21.670	0.40

(iii) L-isoleucine in aqueous KCl solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
303.15	17.14	-12.220	0.50
308.15	27.47	-16.670	0.40
313.15	44.80	-27.200	0.50
318.15	34.87	-16.550	0.30
323.15	35.15	-15.910	0.30

(iv) L-proline in aqueous K2SO4 solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
303.15	0.10	-0.510	0.30
308.15	-0.77	-0.230	0.20

313.15	3.27	-0.430	0.40
318.15	4.54	-0.520	0.40
323.15	7.06	-0.830	0.40

(v) L-proline in aqueous KNO3 solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
303.15	-4.64	0.140	0.10
308.15	8.40	-1.240	0.30
313.15	11.24	-1.490	0.40
318.15	13.01	-1.570	0.40
323.15	12.86	-1.470	0.40

(vi) L-proline in aqueous KCl solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
298.15	15.91	-1.880	0.60
303.15	11.06	-1.380	0.50
308.15	8.09	-0.970	0.50
313.15	0.22	0.010	0.10
318.15	2.71	-0.150	0.10
323.15	4.94	-0.260	0.20

(vii) L-glutamine in aqueous K2SO4 solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
303.15	-3.13	-4.490	0.40
308.15	-6.96	-2.040	0.40
313.15	13.45	-9.430	0.60
318.15	8.94	-7.120	0.50
323.15	9.71	-6.800	0.50

(viii) L-glutamine in aqueous KNO3 solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
303.15	-36.22	7.610	0.40

308.15	-12.83	-2.080	0.40
313.15	7.71	-8.650	0.50
318.15	18.56	-11.210	0.30
323.15	15.61	-8.620	0.20

(ix) L-glutamine in aqueous KCl solution

Temperature (K)	$\varphi_k^0 \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)	$S_k \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-2}\ kg$)	$\sigma \times 10^{11}$ ($bar^{-1}\ m^3\ mol^{-1}$)
303.15	19.35	-10.270	0.50
308.15	5.02	-3.750	0.30
313.15	10.44	-6.540	0.40
318.15	-4.20	1.220	0.30
323.15	-1.38	-0.290	0.20

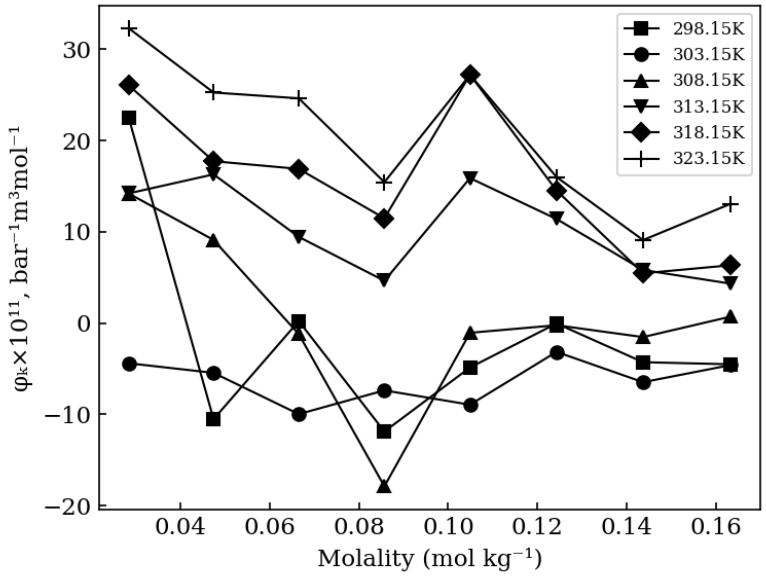


Fig.3.10: Plot of apparent molal isentropic compressibility versus concentration of L-isoleucine in aqueous K2SO4 solution.

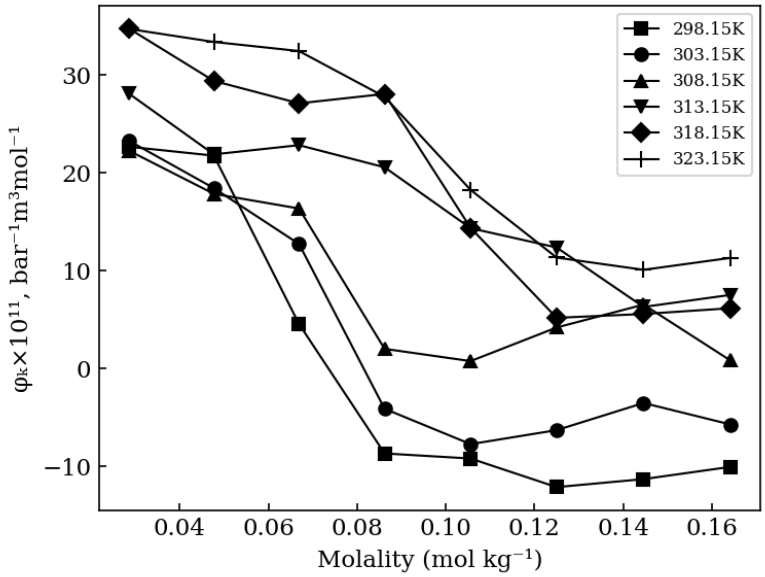


Fig.3.11: Plot of apparent molal isentropic compressibility versus concentration of L-isoleucine in aqueous KNO3 solution.

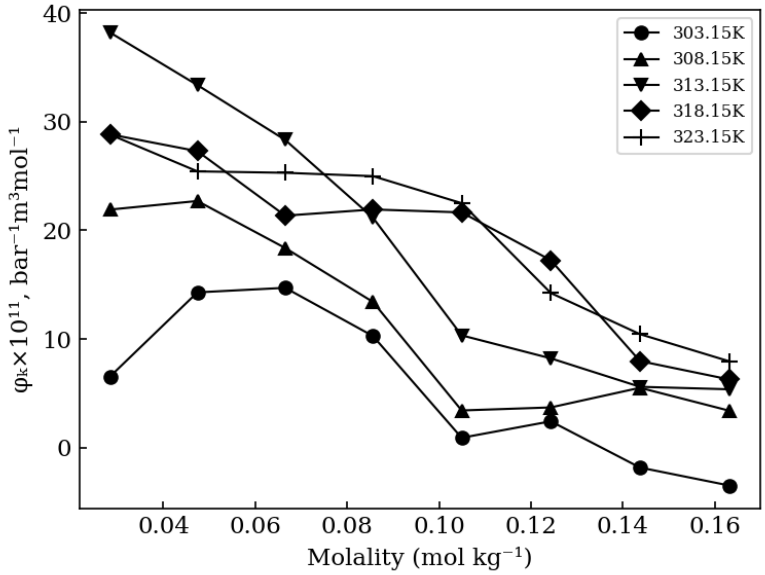


Fig.3.12: Plot of apparent molal isentropic compressibility versus concentration of L-isoleucine in aqueous KCl solution.

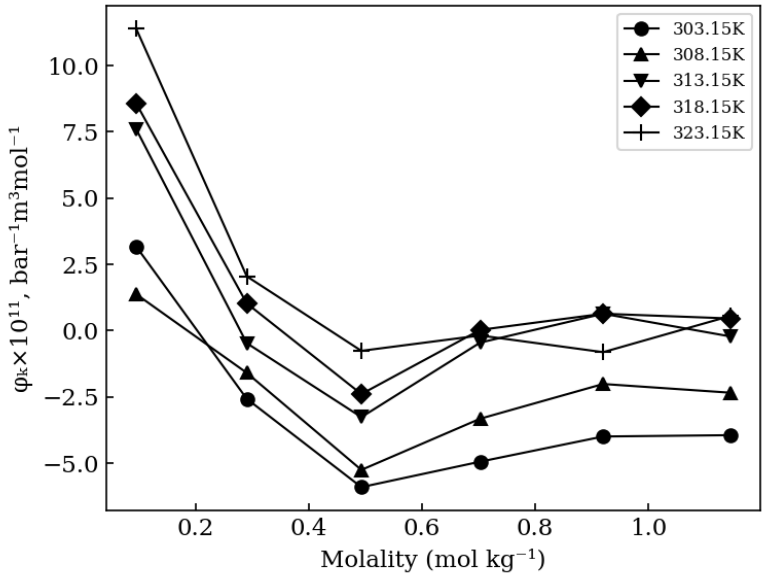


Fig.3.13: Plot of apparent molal isentropic compressibility versus concentration of L-proline in aqueous K2SO4 solution.

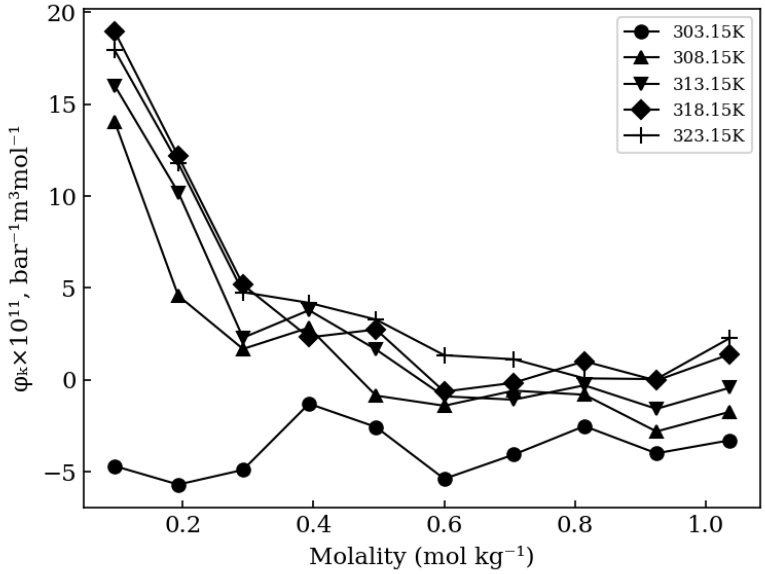


Fig.3.14: Plot of apparent molal isentropic compressibility versus concentration of L-proline in aqueous KNO3 solution.

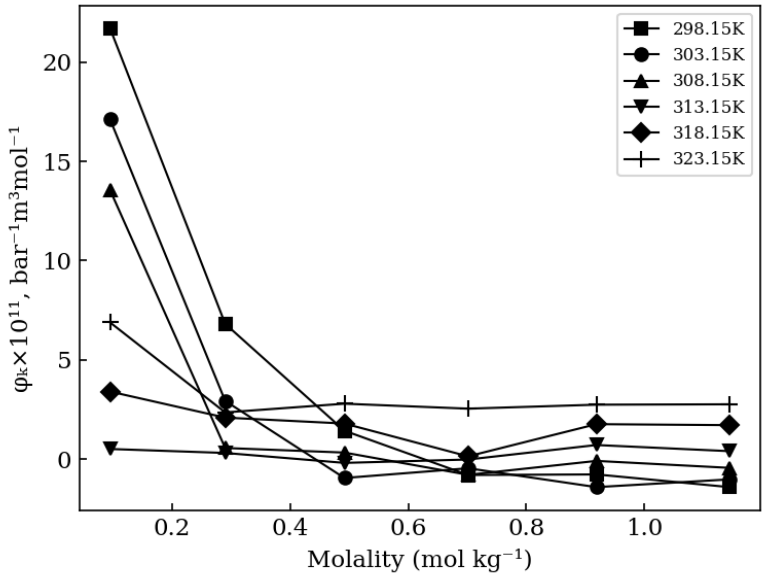


Fig.3.15: Plot of apparent molal isentropic compressibility versus concentration of L-proline in aqueous KCl solution.

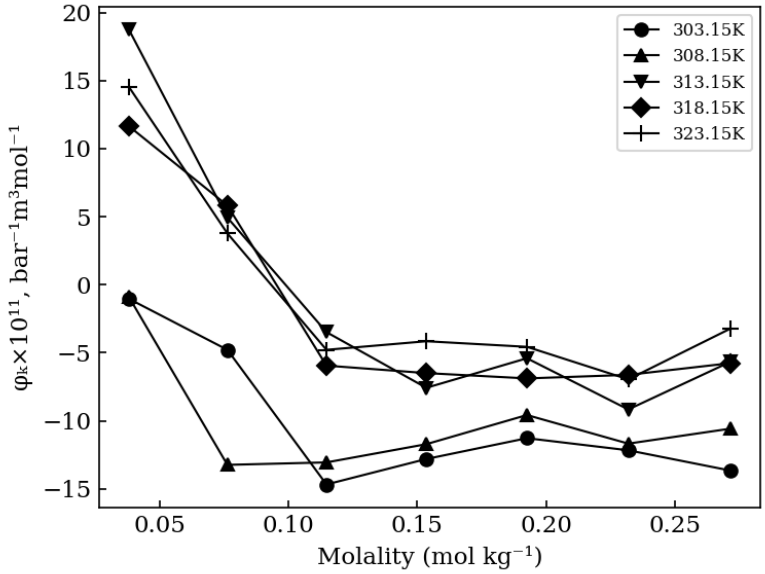


Fig.3.16: Plot of apparent molal isentropic compressibility versus concentration of L-glutamine in aqueous K2SO4 solution.

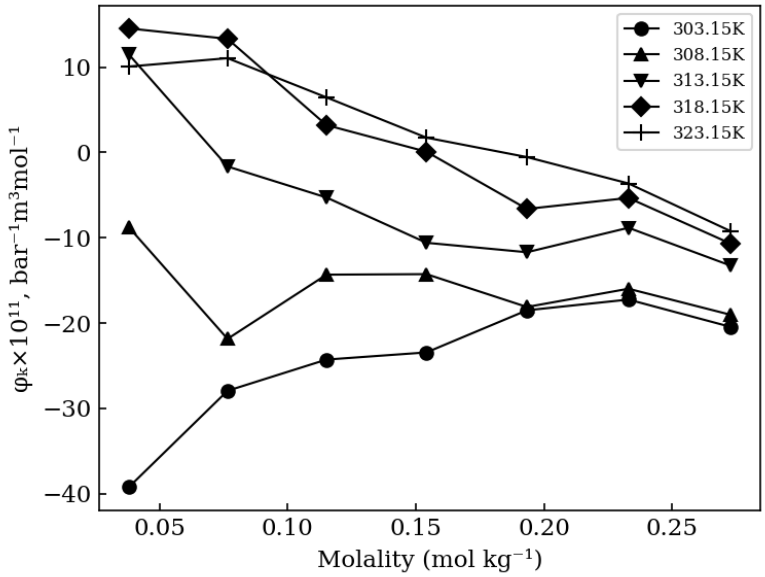


Fig.3.17: Plot of apparent molal isentropic compressibility versus concentration of L-glutamine in aqueous KNO3 solution.

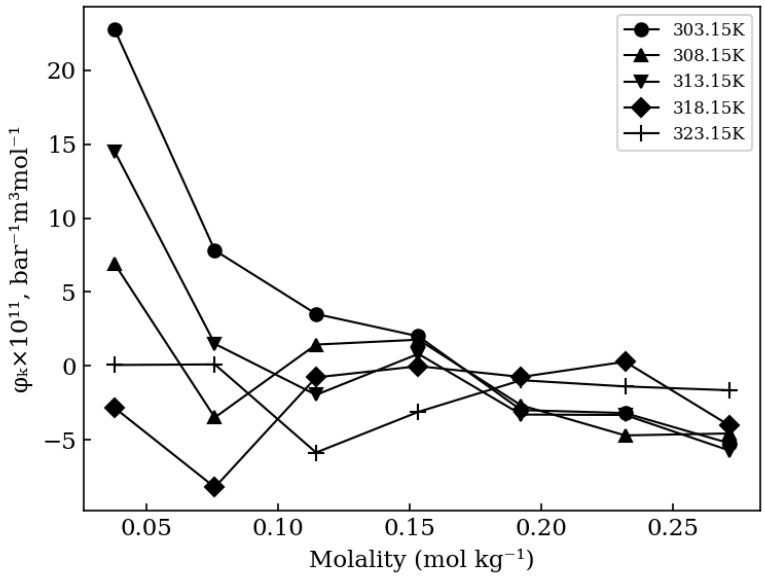


Fig.3.18: Plot of apparent molal isentropic compressibility versus concentration of L-glutamine in aqueous KCl solution.

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