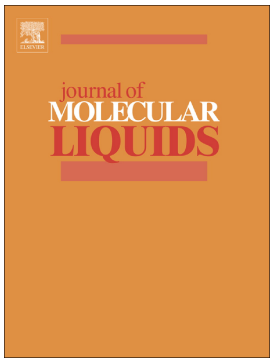

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Exploration of the solvation behavior of the synthesized 1-hexyl-3-methylimidazolium bromide [C_6mim][Br] ionic liquid with L-cysteine and N-acetyl L-cysteine) in aqueous medium at different temperatures

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Abstract

The interactions of L-cysteine and N-acetyl L-cysteine with imidazolium-based ionic liquid 1-hexyl-3-methylimidazolium bromide [C_6mim] [Br] as a function of temperature have been studied by a combination of volumetric and acoustic properties. Densities and speeds of the sound of L-cysteine and N-acetyl L-cysteine in (0.00, 0.005, 0.01, 0.03 and 0.05) mol.kg^{-1} aqueous solutions of 1-hexyl-3-methylimidazolium bromide have been measured at T = (288.15, 298.15, 308.15 and 318.15) K. From density data, the apparent molar volume (V_ϕ) the partial molar volume (V_ϕ^0) and standard partial molar volumes of transfer (ΔV_ϕ^0) for L-cysteine and N-acetyl L-cysteine from water to aqueous 1-hexyl-3-methylimidazolium bromide solutions have been calculated. Partial molar isentropic compression ($K_{\phi,s}$) and partial molar isentropic compression of transfer ($\Delta K_{\phi,S}^0$) have been calculated from the speed of sound data. The pair and triplet interaction coefficient have been calculated from both these properties. The parameters obtained have been used to describe the results in terms of (solute-solute), (solute-solvent) interactions, structure building and structure floating behaviour of amino acids in aqueous 1-hexyl-3-methylimidazolium bromide solutions.

Keywords: L-cysteine; N-acetyl L-cysteine; 1-hexyl-3-methylimidazolium bromide [C_6mim][Br]; apparent molar volume; partial molar isentropic compression

Introduction

Thermodynamic parameters of amino acids, as essential structural units of proteins in aqueous electrolyte solutions, deliver important information about solute-solvent and solute–solute interactions that can be of great support in understanding numerous processes, such as protein aggregation, denaturation and protein hydration [1, 2]. Amino acids are biologically important organic compounds that are included of amine (–NH2) and carboxylic acid (–COOH) functional groups, along with a side-chain specific to each amino acid. They play an important role in biotic processes, nutrition supplements, fertilizers, food technology and industry [3]. The study of these compounds in aqueous surroundings can be interesting and useful to enriching our knowledge about their behaviour in a liquid state. The mixture of them with some mixed aqueous solutions give us important information about the effect of additives on biomolecules. In recent years many researchers have done, an interesting job to understand the physicochemical properties of amino acids in aqueous mixed solutions is very and has been done [4-9].

The direct investigations on protein – aqueous interactions are very challenging because of the complex three-dimensional structures of proteins. Therefore, one useful approach, which can help in understanding these interactions, is to study simple compounds such as amino acids, which model some aspects of the protein structure. The thermodynamic properties of amino acids in aqueous electrolyte solutions can provide valuable information regarding the conformational stability of proteins in these solutions, their solubility, folding/unfolding character, solute-solute and solute-solvent interactions [10, 11]. Most important electrolytes, which used as additives in the aqueous amino acids solutions, are ionic liquids (ILs).

Ionic liquids (ILs) have appeared as an innovative class of solvent, which significantly replace conventional, volatile, hurtful organic solvents in chemical and biological processes to equilibrium both commercial and surroundings necessities [12-15]. ILs act as a new class of organic electrolytes which considered as a green and designer solvents because of their unique properties such as excellent solvation ability, negligible vapours pressure, high thermal stability, large liquid range, high hygroscopic ability and large solubility [16, 17].

Ionic liquids as electrolytes play an important role to understand the effect of hydrophobic and electrostatic interactions on the stability of amino acids. Ionic liquids contain bulky cations that are well known to orient the water molecules around them depending upon the size of the alkyl chain. Due to these phenomena, they can influence the physicochemical properties of mixtures,

protein folding/unfolding studies and stability of amino acids [18-19]. Further, is also seen that ionic liquids can be utilized as a suitable medium for carrying out the investigations on the stability of proteins in aqueous solutions [20] and on the other hand it is well known that interactions of the amino acids with water is significant to understand the conformational stability of proteins [21]. To recognize the structural changes of amino acids in aqueous ionic liquid solutions the study of volumetric and acoustic properties plays an important role [22-27] as the more understating about the nature of interactions present the aqueous mixtures of ionic liquids and amino acids can be predicted with help of different parameters obtained from these volumetric and acoustic measurements.

There are various concentration and temperature dependent studies on the measurement and determination of thermodynamic properties/parameters for amino acids with different additives to gain insight about the interactional behavior reported by us and other workers [28-42]. One of the key research areas which attracted researchers is about the protein stability studies in presence of ionic liquids where ionic liquids and amino acids are used in the aqueous biphasic systems. As proteins are greatly affected by the temperature and pressure in aqueous medium and has an important role for establishing the interpretation of facts regarding physical immutability [43] so, the physicochemical properties of mixtures of ionic liquids and amino acids in the aqueous medium is very much important. Thermodynamic studies on the mixtures of amino acids with ionic liquids have not been carried out to much extent [44-51]. In other words, systematic studies on volumetric and acoustic properties of amino acids and ionic liquids (ILs) to understand the effect of anionic/ cationic chain length of the ILs are still very limited.

In view of this, in the present manuscript we have attempted to get an overall idea on the volumetric and acoustic properties of L-cysteine and N acetyl L- cysteine and in the aqueous solutions of ionic liquid 1-hexyl-3-methylimidazolium bromide been measured at T = (288.15, 298.15, 308.15 and 318.15) K. Experimental densities have been used to obtain the apparent molar volume (V_ϕ), the partial molar volume (V_ϕ^0) and standard partial molar volumes of transfer (ΔV_ϕ^0). The partial molar volume provides information about solute-solvent interactions. The partial molar volumes of transfer give qualitative as well as quantitative information regarding solute-solvent interactions without taking into account the effects of solute-solute interactions.

The limiting apparent molar expansivities ϕ_E^0 is an important tool to understand the solute-solvent interactions the sign of ($\partial\phi_E^0$ / ∂T) provide the information whether the solute having structure making or structure breaking capacity. The speed of sound data is used to calculate partial molar isentropic compression ($K_{\phi,s}$) and partial molar isentropic compression of transfer ($\Delta K_{\phi,S}^0$). The apparent molar isentropic compression delivers insight on whether the water molecules around ionic charged groups of amino acids are more or less compressible than water molecules in the bulk solution. This also indicates that water molecules around solute are more or less ordered

2. EXPERIMENTAL

2.1 Materials: - Reagents used for synthesis of 1-hexyl-3-methylimidazolium bromide are 1-methyl imidazole (> 99%), 1- bromohexane (> 99%), acetonitrile (> 99%), hexane (> 99%), L-cysteine (> 99%) and N-acetyl L-cysteine (> 99%). These reagents were used without further purification. Freshly prepared triple distilled and degassed water having specific conductance of < 10^{-6} S·cm^{-1}was used for the preparation of solutions. Table 1 represent the specifications of material used.

2.2 Synthesis of ionic liquid 1-hexyl-3-methylimidazolium bromide [C_6mim] [Br]

1-hexyl-3-methylimidazolium bromide was prepared and purified by using the procedure described in the literature [52, 53]. Briefly, 1-hexyl-3-methylimidazolium bromide was synthesized by direct alkylation of 1-methylimidazole in acetonitrile with an excess of 1-bromohexane in a round bottom flask at T = 353.15 K for 48 hours under a nitrogen atmosphere. The completion of the reaction was monitored by thin layer chromatography. Once the reaction was completed, the product was dried in high vacuum at T = 333.15 K using a rotary evaporator (Heidolph, Type: Basis Hei-VAP ML, 50/60 Hz) for at least 3 hours in 0.7 kPa. The obtained ionic liquid is hygroscopic in nature. Thus, volumetric Karl Fischer analysis (Esico International microprocessor Karl Fischer) moisture titrator with highly sensitive motorized dispensing system was employed to determine the water content. The water content found by Karl Fischer method in the 1-hexyl-3-methylimidazolium bromide was less than mass fraction 0.05. Ionic liquid was analysed by using ^{1}H NMR (Bruker 400 MHz) and FTIR (Agilent Carry 630) spectroscopic studies to confirm the absence of any major impurities and they were found to be in good

agreement with those reported in the literature [54, 55]. The obtained ionic liquid has purity greater than mass fraction 0.98 on the basis of spectral data. The supporting information regarding the spectra are given in figure S1.

2.3 Apparatus and procedure: The solutions were prepared in glass vails in molal base concentration by using Sartorius CPA 225 D balance having a precision of ±0.00001g. The uncertainties in the molality of solutions are within ± 2×10^{-5} mol·kg^{-1}. The density measurements were made on Anton Paar Density. DSA 5000M densimeter. The speed of sound was measured using a propagation time technique. The sample is sandwiched between two piezoelectric ultrasound transducers. One transducer emits sound waves through the sample-filled cavity at a frequency of approximately 3 MHz; the second transducer receives those waves. Thus, the speed of sound is obtained by dividing the known distance between the transmitter and receiver by the measured propagation time of the sound wave. Thus, the speed of sound is obtained by dividing the known distance between the transmitter and receiver by the measured propagation time of the sound wave [56]. A density check or an air/water adjustment was performed at 293.15 K with triply distilled, degassed water, and with dry air at atmospheric pressure. Before each series of measurements, the densimeter was calibrated with triple distilled and degassed water, in the experimental temperature. The sensitivity of the instrument corresponds to precision in density and speed of sound measurements of 1×10^{-3} kg·m^{-3} and 1×10^{-2} m·s^{-1}. The standard uncertainty of the density and speed of sound estimates was found to be within ± 0.005 kg·m^{-3} and ± 0.05 m·s^{-1}, respectively.

3. RESULTS AND DISCUSSION

3.1 Density measurements

3.1.1 Apparent Molar Volume

The experimental value of solution densities, ρ for L-cysteine and N acetyl L-cysteine in (0.00, 0.005, 0.01, 0.03 and 0.05) mol.kg^{-1} aqueous solutions of 1-hexyl-3-methylimidazolium bromide were measured at T = (288.15, 298.15, 308.15 and 318.15) K. These values of densities were used to calculate apparent molar volumes (V_ϕ) using the following equation:

$$V_\phi = [(M/\rho) - \{(\rho-\rho_0)/(m_A\rho\rho_0)\}] \quad (1)$$

Where m_A *i*s the molality (mol·kg^{-1}) amount of solute i.e. amino acids per 1 kg of the solvent (1-hexyl-3-methylimidazolium bromide + water), M is the molar mass of solute (kg·mol^{-1}), ρ_0 and ρ are the densities (kg·m^{-3}) of the solvent and solution. The values of densities along with apparent molar volumes are reported in table 2. The experimental densities values for (L-cysteine + water and N-acetyl L- cysteine + water) mixtures have been compared with literature values [57, 58] and they are graphically represented in figure 1 and figure 2. By analyzing figure 1 and figure 2 it is observed that experimental densities for (L-cysteine + water and N-acetyl L- cysteine + water) mixtures show the same trend as literature densities i.e. densities values decrease with increase in temperature. The experimental densities values for aqueous ionic liquid (1-hexyl-3-methylimidazolium bromide + water) mixtures also have been compared with literature values [59-62] and graphically represented in figure 3. Figure 3 shows that experimental densities are in good agreement with literature values of densities. The calculated values of the apparent molar volume are graphically represented in figure S1 and figure S2 of supporting information. Figure S2 represents apparent molar volume for L-cysteine in aqueous and aqueous solutions of 1-hexyl-3-methylimidazolium bromide at different temperature while figure S3 represents apparent molar volume for N- acetyl L-cysteine in aqueous and (1-hexyl-3-methylimidazolium bromide + water) mixture at different temperature. Values of apparent molar volume (V_ϕ) for both the amino acids are positive that indicates strong (solute-solvent) interactions and (V_ϕ) increases with increase in temperature for each concentration of amino acids. Besides, the values increase with an increase in the molar mass of amino acids i.e. from L-cysteine to N- acetyl L-cysteine at all concentrations and temperatures of 1-hexyl-3-methylimidazolium bromide, indicating more interactions in N- acetyl L-cysteine as compared to L-cysteine as shown in the scheme.

3.1.2 Partial molar volume

By the least square fitting of apparent molar volume (V_ϕ), the partial molar volume (V_ϕ^0) is calculated by given equation [63].

$$V_\phi = V_\phi^0 + S_V^* m_A \qquad (2)$$

Where V_ϕ^0 is the limiting value of apparent molar volume, S_V^* the experimental slope is the volumetric pairwise interaction coefficient and m_A is the molality (mol·kg^{-1}) of the amino acids

i.e., amount of solute (amino acids) per one kilogram of solvent (a mixture of water + 1-hexyl-3-methylimidazolium bromide). Values of V_ϕ^0 and S_V^* forgiven amino acids in aqueous solutions together with standard errors have reported in table 3 and are graphically represented in figure 4 The values of apparent molar volume V_ϕ^0 for L-cysteine and N-acetyl L-cysteine in water has been compared with the literature [57]. The values V_ϕ^0 are positive and increase with concentration and temperature. The increase in values V_ϕ^0 is described by co-sphere overlap model [64, 65]. The increase in volume is caused by the overlap of co-sphere ionic species. Positive values V_ϕ^0 are due to the (ion + hydrophobic) interactions. They dominate over (hydrophobic + hydrophobic) interactions those results in volume decrease. At higher temperatures, there is a release of solvation molecules from the solvation layer that results in an increase in volume at infinite dilution. The size of primary and secondary layers also plays an important role to explain the increase in volume. Formation of zwitterion species in the solution leads to (zwitterion + solvent) and (zwitterion + zwitterion) interactions at infinite dilution. At higher temperature, there is an expansion of solution caused by the release of some solvent from the solvation layer into the solution. Also with the increase in molar mass the magnitude of V_ϕ^0 increases form L-cysteine to N-acetyl L-cysteine. From table 3, it is observed that value S_V^* are negative for all concentrations of 1-hexyl-3-methylimidazolium bromide at all temperatures. The negative values indicate that it is weak (solute + solute) interactions in the solutions of amino acids and 1-hexyl-3-methylimidazolium bromide. Since there is no specific trend in the values of S_V^*, this means (solute + solute) interactions are also affected by other factors [66]. Larger values of V_ϕ^0 as compared to S_V^* indicate that (solute + solvent) interactions are more dominate over (solute + solute) interactions.

3.1.3 Partial molar volume of transfer

Transfer volume of L-cysteine and N-acetyl L-cysteine from water to aqueous 1-hexyl-3-methylimidazolium bromide solutions at infinite dilution was calculated by using the equation (3)

$\Delta V_\phi^0 = V_\phi^0$ (in aqueous 1-hexyl-3-methylimidazolium bromide solution) - V_ϕ^0 (in water) (3)

The calculated values of partial molar volume of transfer as reported in table S1 of supporting information. All the values are positive and increase with an increase in concentrations of 1-hexyl-3-methylimidazolium bromide for both amino acids. Positive values of ΔV_{ϕ}^{0} suggesting strong (ion + ion) interactions of 1-hexyl-3-methylimidazolium bromide with amino acids. The presence of polar groups in the structure moiety of ionic liquid and amino acids leads to structure maker ability of solute in the solutions. Hence positive values of ΔV_{ϕ}^{0} suggests structural making ability of solute which is due to the structural interactions of two co-spheres according to co-sphere model [64,65]. Depending upon co-sphere overlap model regarding the values of ΔV_{ϕ}^{0}, they provide information regarding (solute + solvent) interactions. There are negligible (solute + solute) interactions as compared to (solute + solvent) interactions as the magnitude of ΔV_{ϕ}^{0} is positive. Various types of interactions present between amino acids and ionic liquid molecules can be defined as (a) (ion + hydrophobic) interactions (b) (hydrophilic + hydrophilic) interactions, (c) (ion-hydrophobic) interactions and (d) (hydrophobic + hydrophobic) interactions. According to co-sphere overlap model, ion-hydrophobic interactions and hydrophobic-hydrophobic interactions contribute negatively whereas ion-hydrophilic and hydrophilic-hydrophilic interactions contribute positively to the ΔV_{ϕ}^{o} values. Positive values of the transfer parameters indicate that ion–hydrophilic and hydrophilic – hydrophilic interactions are dominating over ion-hydrophobic and hydrophobic + hydrophobic interactions in the present study. Because the addition of co-solute to the aqueous solution of 1-hexyl-3-methylimidazolium bromide destroys the cage structure of the solvent and solute. Hence the positive data for the partial molar volume of transfer reflects that ion-ion or solute – solute interactions are dominating in amino acids + 1-hexyl-3-methylimidazolium bromide + water system and have the structure-making nature.

3.1.4 Temperature-dependent partial molar volume

The variation of apparent molar volumes at infinite dilution with the temperature can be studied by the general polynomial equation as given

$$V_{\phi}^{0} = a + b\,(T - T_{ref}) + c\,(T - T_{ref})^{2} \qquad (4)$$

Where T is the temperature in Kelvin. T_{ref} = 298.15 K. a, b, and c are empirical constants. The values of empirical constants for L-cysteine and N-acetyl L-cysteine in aqueous of 1-hexyl-3-methylimidazolium bromide have been reported in table 4. The coefficient c has positive values for all amino acids except in case of (L-cysteine + 0.00 mol.kg^{-1} 1-hexyl-3-methylimidazolium bromide) has a negative value. The theoretical V_ϕ^o values were calculated by using the parameters mentioned in table 4. The deviations obtained from experimental V_ϕ^o and theoretical V_ϕ^o values have been reported in table 4. The ARD (σ) deviations are calculated by using the equation (5) given as follows:

$$\sigma = (1/n)\Sigma[abs((Y_{\exp tl.} - Y_{calc.})/Y_{\exp tl.})] \quad (5)$$

Where Y = V_ϕ^o (apparent molar volume at infinite dilution). The small values of deviations reported in table 4 indicate that the polynomial equation fits very well in the present study of ionic liquid and amino acids. The temperature dependence of partial molar volume at infinite dilution (V_ϕ^o) can be expressed in terms of the absolute temperature (T). The limiting apparent molar expansibilities are calculated by using the relation given in Equation (6),

$$\phi_E^0 = (\partial V_\phi^0/\partial T)_p = b + 2\,c\,(T - T_{ref}) \quad (6)$$

The limiting apparent molar expansibilities at infinite dilution $\phi_E^0 = (\partial V_\phi^0/\partial T)_p$ deliver valuable information about the (solute + solvent) interactions present in the solution [67, 68]. To understand the structure making and structure breaking ability of solute in the mixed solvent system Hepler [69] developed a thermodynamic expression as given

$$(\partial \phi_E^0/\partial T)_p = (\partial^2 V_\phi^o/\partial T^2)_p = 2c \quad (7)$$

The values of limiting apparent molar expansibilities ϕ_E^0 and $(\partial \phi_E^0/\partial T)_p$ are reported in table S2 of supporting information. The ϕ_E^0 values are found to be positive at all temperature and concentrations of 1-hexyl-3-methylimidazolium bromide. The positive values suggest the presence of (solute + solvent) interactions in the system. Parameter $(\partial \phi_E^0/\partial T)_p$ determines the tendency of dissolved solute as a structure maker or structure breaker in a solvent. Positive values for $(\partial \phi_E^0/\partial T)_p$ suggests structure making capacity whereas negative values for $(\partial \phi_E^0/\partial T)$

suggests structure breaking of solutes [70, 71]. The ϕ_E^0 values show an irregular trend with an increase in concentrations of the ionic liquid. This is due to the packing or caging effects, which also provide information about interactions present in the system [72, 73]. The positive and negative values of $(\partial \phi_E^0/\partial T)$ for both the amino acids shows the structure making capacity of amino acids in the system.

3.2 Speed of sound measurements

3.2.1 Apparent molar isentropic compression

The experimental value of the speed of sound u for L-cysteine and N acetyl L-cysteine in (0.00, 0.005, 0.01, 0.03 and 0.05) mol.kg^{-1} aqueous solutions of 1-hexyl-3-methylimidazolium bromide were measured at T = (288.15, 298.15, 308.15 and 318.15) K. Experimental data of speed of sound were used to calculate apparent molar isentropic compression ($K_{\phi,s}$) for L-cysteine and N acetyl L-cysteine in aqueous solutions of 1-hexyl-3-methylimidazolium bromide at different temperatures by using the following equation

$$K_{\phi,s} = [(M\kappa_S/\rho) - \{(\kappa_S\rho_0 - \kappa_{S,0}\rho)/(m_A\rho\rho_0)\}] \quad (8)$$

where m_A is the molality (mol·kg^{-1}) of the solution *i.e.* amount of solute (amino acids) per one kilogram of solvent (a mixture of water + 1-hexyl-3-methylimidazolium bromide), M is the molar mass of the solute (kg·mol^{-1}) and ρ_0 and ρ are the densities (kg·m^{-3}) of the solvent and solution. $\kappa_{S,0}$ and κ_S are the isentropic compressibility of pure solvent and solution, respectively. The coefficient of isentropic compressibility κ_S, calculated using the relation

$$\kappa_S = 1/(c^2\rho) \quad (9)$$

where c is the speed of sound and ρ is the density of the solution.

The experimental speed of sound data for aqueous solutions of L-cysteine and N-acetyl L-cysteine have been compared with literature [57] values of speed of sound data and are graphically represented in figures 5 and figure 6. From figures 5 and figure 6, it is observed that experimental and literature [57] speed of sound values are in good agreement. Further, the experimental speed of sound values for (water + 1-hexyl-3-methylimidazolium bromide) mixtures have been compared with the literature [60] values and are represented in figure 7. The

values are in good agreement with each other. The experimental values for the speed of sound along with apparent molar isentropic compression are reported in table 5 and graphically represented in figure S4 and figure S5 of supporting information. From the data, it is observed that values of apparent molar isentropic compression ($K_{\phi,s}$) are negative at all temperatures and concentrations of 1-hexyl-3-methylimidazolium bromide. The negative values of apparent molar isentropic compression ($K_{\phi,s}$) decrease with increase in the temperature and concentrations of 1-hexyl-3-methylimidazolium bromide. The negative values show that water molecules are less compressible around the ionic charged species of amino acids as compared to water molecules in the bulk that indicate greater loss of structural compressibility of water suggesting a superior gathering significance by the solute on the solvent.

3.2.2 Partial molar isentropic compression

The variation of the apparent molar isentropic compression $K_{\phi,s}$ with the molal concentration can be examined by the equation (10):

$$K_{\phi,s} = K^0_{\phi,s} + S^*_K m_A \quad (10)$$

where $K^0_{\phi,s}$ is the limiting isentropic compression and S^*_K is the experimental slope, which specifies (solute-solute) interactions, m_A is the molality of the amino acids in aqueous 1-hexyl-3-methylimidazolium bromide solution. Table 6 represents the values of limiting isentropic compression $K^0_{\phi,s}$ and experimental slope S^*_K together with standard error derived by the least-squares fitting. The calculated values $K^0_{\phi,s}$ for L-cysteine and N-acetyl L-cysteine are graphically represented in figure 8. Negative values of $K^0_{\phi,s}$ for amino acids at low temperature attributed the strong interactions between water molecules and amino acids [74, 75]. At higher temperature values of $K^0_{\phi,s}$ becoming less negative that indicates a reduction in force of attractions between water molecules and amino acids and some water molecules are released to bulk. The values of S^*_K are negative that specifies (solute + solute) interactions are negligible at infinite dilution and (solute + solvent) interactions are prevailing in the mixture [75, 76].

3.2.3 Partial molar isentropic compression of transfer

The partial molar isentropic compression of transfer $\Delta K^0_{\phi,S}$ of each amino acids from water to aqueous 1-hexyl-3-methylimidazolium bromide solutions at infinite dilution were calculated by using the equation

$$\Delta K^0_{\phi,S} = K^0_{\phi,s} \text{ (in aqueous 1-hexyl-3-methylimidazolium bromide) - } K^0_{\phi,s} \text{ (in water)} \quad (11)$$

The calculated values $\Delta K^0_{\phi,S}$ by using equation (11) are reported in table S3 of supporting information are positive for L-cysteine and N-acetyl L- cysteine at all concentrations and temperature of 1-hexyl-3-methylimidazolium bromide. From the table, it indicates that $\Delta K^0_{\phi,S}$ values increase with the increase in the concentration of 1-hexyl-3-methylimidazolium bromide.. The positive values of $\Delta K^0_{\phi,S}$ specifying the domination of interactions between the zwitterionic centre of amino acids and 1-hexyl-3-methylimidazolium bromide signifying the structure building affinity of the ions. The interaction between the zwitterionic center of amino acids and 1-hexyl-3-methylimidazolium bromide increase with increasing the concentration of 1-hexyl-3-methylimidazolium bromide [77, 78]. In other words, from the obtained values it is concluded that with increase in concentration of 1-hexyl-3-methylimidazolium bromide and temperature the structure making tendency of ions increase leading to interaction between amino acids and 1-hexyl-3-methylimidazolium bromide.

3.2.4 Pair and triplet interaction coefficients

To understand the solute-solute interactions, McMillan and Mayer theory [79], which was further discussed, by Friedman and Krishanan [80] proposed an equation to calculate the interaction coefficient. Partial molar volume of transfer and partial molar isentropic compression of transfer can be expressed using equation (12) and (13)

$$\Delta V^0_\phi \text{(water to aqueous [C}_6\text{mim][Br] solution)} = 2\, V_{AB}\, m_B + 3\, V_{ABB}\, m_B^2 \quad (12)$$

$$\Delta K^0_{\phi,S} \text{(water to aqueous [C}_6\text{mim][Br] solution)} = 2\, K_{AB}\, m_B + 3\, K_{ABB}\, m_B^2 \quad (13)$$

where *A* denotes amino acid, *B* denotes ionic liquid (1-hexyl-3-methylimidazolium bromide) and m_B is the molality of ionic liquid (1-hexyl-3-methylimidazolium bromide). The corresponding parameters V_{AB}, V_{ABB} for volume and K_{AB}, K_{ABB} for adiabatic compressibility denote pair and

triplet interaction coefficients. These constants were calculated by fitting the ΔV_{ϕ}^{0} and $\Delta K_{\phi,S}^{0}$ values to equation (12) and (13). The values of pair and triplet interaction coefficients are reported in table S4 of supporting information. The values of V_{AB} are positive for both L-cysteine and N-acetyl L-cysteine at all temperatures whereas V_{ABB} is negative and positive for both amino acids. The positive values of V_{AB} predict the pairwise interaction among amino acids and 1-hexyl-3-methylimidazolium bromide. The positive values of K_{AB} corresponding to the compressibility for both amino acids. The triplet coefficient K_{ABB} is negative as well as positive for both amino acids at all temperatures. The positive values of pair interaction coefficients V_{AB} as compared to negative values of V_{ABB} for L-cysteine and N-acetyl L-cysteine propose that interactions occur due to the overlap of hydration spheres of (solute + co-solute) molecules. The positive values of pair interaction coefficient for volumetric and compressibility measurements indicate that pairwise interactions are ruling in the (amino acid + 1-hexyl-3-methylimidazolium bromide + water) mixtures [81].

4. Conclusion

Thermodynamic study of volumetric and acoustic properties was carried out for L-cysteine and N-acetyl L-cysteine in aqueous 1-hexyl-3-methylimidazolium bromide solutions at different concentrations and temperatures. Density and speed of sound measurements provide evidence about the interactions that may occur in the mixtures. Apparent molar properties and partial molar properties indicate the presence of strong solute-solvent interactions in the ternary system. The magnitude of interactions increases with an increase in the molar mass of amino acids and an increase in the concentration of 1-hexyl-3-methylimidazolium bromide solution. The solute-solvent interactions increase from L-cysteine to N-acetyl L-cysteine. The second derivative of temperature $(\partial^2 V_{\phi}^{o} / \partial T^2)_p$ provides information about the structure making property of amino acids in aqueous 1-hexyl-3-methylimidazolium bromide solution. From the outcomes, it is determined that ion–hydrophilic and hydrophilic–hydrophilic interactions seem to be dominating over hydrophobic–hydrophobic and ion–hydrophobic interactions in the ternary system with the domination of solute-solvent interactions in the system.

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Scheme 1 Amino acids and 1-hexyl-3-methylimidazolium bromide interactions.

Figure 1 Plots of experimental and literature [57, 58] values of densities for (L-cysteine + water) mixtures at different temperatures.

Figure 2 Plots of experimental and literature [57] values of densities for (N-acetyl L-cysteine + water) mixtures at different temperatures.

Figure 3 Plots of experimental and literature [59-62] values of densities for (1-hexyl-3-methylimidazolium bromide + water) mixtures at different temperatures (a) 288.15 K (b) 298.15 K (c) 308.15 K.

Figure 4 Plots of apparent molar volume at infinite dilution (V_{ϕ}^{0}) (a) L-cysteine (b) N-acetyl L-cysteine in aqueous 1-hexyl-3-methylimidazolium bromide solutions at different temperatures.

Figure 5 Plots of experimental and literature [57] values of speed of sound for (L-cysteine + water) mixtures at different temperatures.

Figure 6 Plots of experimental and literature [57] values of speed of sound for (N-acetyl L-cysteine + water) mixtures at different temperatures.

Figure 7 Plots of experimental and literature [60] values of speed of sound for (1-hexyl-3-methylimidazolium bromide + water) mixtures at different temperatures (a) 288.15 K (b) 298.15 K (c) 308.15 K.

Figure 8 Plots of limiting isentropic compression ($K_{\phi,s}^{0}$) (a) L-cysteine (b) N-acetyl L-cysteine in aqueous 1-hexyl-3-methylimidazolium bromide solutions at different temperatures.

Table 1

Specifications of chemicals used

Chemicals Name	CAS No	Suppliers	Molar mass($g \cdot mol^{-1}$)	Mass Fraction Purity[#]
L-cysteine	52-90-4	Merck, Germany	121.16	≥0.99
N-acetyl L-cysteine	616-91-1	Merck, Germany	163.2	≥0.99
1-methylimidazole	616-47-7	Merck, Germany	82.10	≥0.99
1-bromohexane	111-25-1	HiMedia Laboratories Pvt. Ltd., Mumbai, India	165.07	≥0.99
Acetonitrile	75-05-8	LOBA Chemie Pvt. Ltd., Mumbai India	41.05	≥0.99
Hexane	110-54-3	TCI Pvt. Ltd	86.18	≥0.99
1-hexyl-3methylimidazolium bromide	85100-78-3	Synthesized in lab	247.18	>0.98*

[#] as declared by the supplier, * on the bases of spectroscopic analysis (IR and NMR)

Table 2

Values of densities ρ and apparent molar volumes V_ϕ of L-cysteine and N-acetyl L-cysteine in aqueous solutions of 1-hexyl-3-methylimidazolium bromide at different temperatures and experimental pressure p = 0.1 MPa.

[a]m_A	$\rho \times 10^{-3}$ / (kg·m^{-3})				$V_\phi \times 10^6$ / (m^3·mol^{-1})			
/(mol·kg^{-1})	T=288.15 K	T=298.15 K	T=308.15 K	T=318.15 K	T=288.15 K	T=298.15 K	T=308.15 K	T=318.15 K
			L-Cysteine + 0.00 mol·kg^{-1} [C$_6$mim][Br]					
0.00000	0.999108	0.997046	0.994037	0.990216				
0.09925	1.003793	1.001731	0.998725	0.994909	73.64	73.69	73.74	73.79
0.19669	1.008392	1.006330	1.003327	0.999516	73.30	73.36	73.40	73.45
0.29859	1.013201	1.011139	1.008139	1.004333	72.95	73.01	73.05	73.10
0.40044	1.018009	1.015947	1.012950	1.009149	72.61	72.66	72.71	72.75
0.49783	1.022606	1.020544	1.017559	1.013753	72.28	72.33	72.38	72.42
0.59624	1.027251	1.025189	1.022197	1.018406	71.96	72.01	72.05	72.09
0.69817	1.032062	1.030000	1.027012	1.023225	71.62	71.67	71.71	71.75
			L-Cysteine + 0.005 mol·kg^{-1} [C$_6$mim][Br]					
0.00000	0.999459	0.997282	0.994272	0.990421				
0.09953	1.004152	1.001975	0.998970	0.995119	73.68	73.74	73.76	73.86
0.20096	1.008934	1.006757	1.003758	0.999907	73.33	73.39	73.41	73.51
0.30044	1.013625	1.011448	1.008453	1.004602	72.99	73.05	73.07	73.17
0.39702	1.018179	1.016002	1.013011	1.009160	72.66	72.72	72.74	72.84

0.50209	1.023133	1.020956	1.017971	1.014120	72.31	72.37	72.39	72.48
0.59963	1.027732	1.025555	1.022575	1.018724	71.99	72.04	72.06	72.15
0.69078	1.032329	1.029852	1.026877	1.023426	71.69	71.74	71.76	71.85
			L-Cysteine + 0.01 mol·kg^{-1} [C_6mim][Br]					
0.00000	0.999899	0.997512	0.994450	0.990626				
0.09778	1.004505	1.002118	0.999060	0.995236	73.72	73.79	73.82	73.92
0.19770	1.009211	1.006824	1.003772	0.999948	73.38	73.44	73.47	73.57
0.29943	1.014002	1.011615	1.008568	1.004744	73.03	73.09	73.12	73.22
0.40108	1.018790	1.016403	1.013361	1.009537	72.69	72.75	72.77	72.87
0.50207	1.023546	1.021159	1.018122	1.014298	72.35	72.41	72.43	72.53
0.59443	1.027896	1.025509	1.022477	1.018653	72.05	72.10	72.13	72.22
0.70079	1.032906	1.030519	1.027492	1.023668	71.70	71.75	71.77	71.86
			L-Cysteine + 0.03 mol·kg^{-1} [C_6mim][Br]					
0.00000	1.000559	0.998132	0.995397	0.991446				
0.10096	1.005304	1.002877	1.000147	0.996196	73.79	73.85	73.88	73.99
0.19737	1.009835	1.007708	1.004683	1.000732	73.46	73.52	73.55	73.65
0.30194	1.014750	1.012623	1.009603	1.005652	73.11	73.16	73.19	73.29
0.40114	1.019413	1.017286	1.014271	1.010320	72.77	72.83	72.85	72.95
0.51424	1.024728	1.022601	1.019592	1.015641	72.40	72.45	72.47	72.57
0.60874	1.029170	1.027043	1.024038	1.020087	72.08	72.14	72.16	72.25

0.69922	1.033422	1.031295	1.028295	1.024344	71.79	71.84	71.86	71.95
L-Cysteine + 0.05 mol·kg^{-1} [C_6mim][Br]								
0.00000	1.001519	0.99935	0.996297	0.992266				
0.09959	1.006195	1.004021	1.000968	0.996937	73.82	73.93	74.01	74.12
0.19667	1.010752	1.008575	1.005522	1.001491	73.49	73.59	73.67	73.78
0.30020	1.015613	1.013431	1.010378	1.006347	73.14	73.24	73.32	73.42
0.40158	1.020373	1.018186	1.015133	1.011102	72.80	72.90	72.98	73.08
0.50010	1.024999	1.022807	1.019754	1.015723	72.47	72.57	72.65	72.75
0.59788	1.029589	1.027394	1.024341	1.020310	72.15	72.25	72.32	72.42
0.69436	1.034119	1.031919	1.028866	1.024835	71.83	71.93	72.00	72.10
N-Acetyl L-Cysteine + 0.00 mol·kg^{-1} [C_6mim][Br]								
0.00000	0.999108	0.997046	0.994037	0.990216				
0.09801	1.003489	1.001329	0.998222	0.994288	118.04	119.20	120.45	121.93
0.20405	1.008229	1.005963	1.002750	0.998694	117.48	118.65	119.90	121.39
0.29892	1.012470	1.010109	1.006801	1.002636	116.99	118.17	119.42	120.91
0.39788	1.016893	1.014433	1.011026	1.006748	116.48	117.66	118.92	120.42
0.50464	1.021665	1.019099	1.015585	1.011184	115.94	117.12	118.39	119.89
0.59896	1.025882	1.023221	1.019613	1.015103	115.46	116.65	117.92	119.43
0.69517	1.030182	1.027425	1.023721	1.019100	114.98	116.17	117.45	118.96
N-Acetyl L-Cysteine + 0.005 mol·kg^{-1} [C_6mim][Br]								

0.00000	0.999359	0.997282	0.994272	0.990420				
0.09902	1.003775	1.001604	0.998495	0.994529	118.12	119.23	120.48	121.96
0.19827	1.008202	1.005936	1.002728	0.998648	117.60	118.72	119.97	121.45
0.29648	1.012582	1.010223	1.006917	1.002724	117.09	118.21	119.47	120.96
0.39760	1.017092	1.014637	1.011230	1.006920	116.57	117.70	118.96	120.45
0.49470	1.021423	1.018876	1.015371	1.010950	116.07	117.21	118.47	119.97
0.59780	1.026021	1.023376	1.019768	1.015229	115.55	116.69	117.96	119.47
0.69278	1.030257	1.027522	1.023819	1.019171	115.08	116.22	117.50	119.01
N-Acetyl L-Cysteine + 0.01 mol·kg^{-1} [C$_6$mim][Br]								
0.00000	0.999899	0.997512	0.994497	0.990630				
0.10118	1.004402	1.001919	0.998802	0.994814	118.17	119.29	120.55	122.08
0.19957	1.008780	1.006205	1.002989	0.998882	117.65	118.78	120.05	121.58
0.29819	1.013168	1.010501	1.007185	1.002960	117.14	118.28	119.55	121.09
0.40024	1.017710	1.014947	1.011527	1.007180	116.62	117.76	119.03	120.58
0.49565	1.021956	1.019103	1.015587	1.011125	116.14	117.28	118.56	120.11
0.59806	1.026513	1.023563	1.019944	1.015360	115.62	116.77	118.05	119.61
0.69937	1.031021	1.027977	1.024255	1.019549	115.11	116.27	117.55	119.12
N-Acetyl L-Cysteine + 0.03 mol·kg^{-1} [C$_6$mim][Br]								
0.00000	1.000560	0.998432	0.995400	0.991450				
0.10082	1.005025	1.002808	0.999672	0.995609	118.32	119.39	120.63	122.12

0.19808	1.009334	1.007029	1.003796	0.999621	117.82	118.89	120.14	121.63
0.29747	1.013737	1.011342	1.008010	1.003721	117.30	118.38	119.64	121.13
0.39883	1.018227	1.015741	1.012308	1.007902	116.79	117.87	119.13	120.63
0.49476	1.022477	1.019905	1.016375	1.011859	116.30	117.39	118.65	120.16
0.60365	1.027301	1.024630	1.020992	1.016351	115.75	116.84	118.11	119.63
0.69732	1.031450	1.028696	1.024963	1.020214	115.29	116.38	117.66	119.18
N-Acetyl L-Cysteine + 0.05 mol·kg^{-1} [C_6Him [Br]								
0.00000	1.001519	0.999352	0.996297	0.992270				
0.10167	1.005992	1.003744	1.000587	0.996449	118.55	119.51	120.76	122.20
0.20044	1.010338	1.008011	1.004756	1.000508	118.04	119.01	120.26	121.71
0.29805	1.014633	1.012228	1.008875	1.004520	117.54	118.51	119.77	121.22
0.40630	1.019396	1.016904	1.013463	1.008969	116.99	117.97	119.23	120.69
0.50017	1.023527	1.020959	1.017404	1.012827	116.52	117.50	118.77	120.23
0.59864	1.027859	1.025213	1.021560	1.016874	116.02	117.01	118.28	119.75
0.69941	1.032293	1.029567	1.025812	1.021016	115.53	116.52	117.79	119.26

[a]m_A is the molality of amino acids in aqueous 1-hexyl-3-methylimidazolium bromide solutions. Standard uncertainties u are $u(\rho) = 5 \times 10^{-3}$ kg·m^{-3}; $u(m) = 2 \times 10^{-5}$ mol·kg^{-1}; $u(T) = 0.001$ K and $u(p) = 0.01$ MPa.

Table 3

Limiting value of apparent molar volume, V_ϕ^0 and experimental slopes, S_v^* of L-cysteine and N-acetyl L-cysteine in aqueous solutions of 1-hexyl-3-methylimidazolium bromide at different temperatures.

[a]m_B / (mol·kg^{-1})	288.15 K	298.15 K	308.15 K	318.15 K
		L-Cysteine		
		$V_\phi^0 \times 10^6$ / (m^3·mol^{-1})		
0.000	73.97(±0.005) 73.96 [31]	74.02(±0.005) 74.01 [31]	74.07(±0.005) 74.05 [31]	74.12(±0.006) 74.17 [31]
0.005	74.01(±0.005)	74.06(±0.005)	74.09(±0.005)	74.20(±0.005)
0.01	74.04(±0.005)	74.11(±0.005)	74.14(±0.005)	74.24(±0.006)
0.03	74.13(±0.005)	74.18(±0.005)	74.22(±0.005)	74.32(±0.005)
0.05	74.15(±0.005)	74.25(±0.005)	74.34(±0.005)	74.45(±0.005)
		$S_V^* \times 10^6$ / (m^3·kg·mol^{-2})		
0.000	-3.37(±0.012)	-3.38(±0.012)	-3.39(±0.012)	-3.41(±0.012)
0.005	-3.37(±0.012)	-3.38(±0.015)	-3.39(±0.012)	-3.41(±0.012)
0.01	-3.36(±0.012)	-3.37(±0.012)	-3.39(±0.012)	-3.40(±0.012)
0.03	-3.36(±0.012)	-3.37(±0.012)	-3.38(±0.012)	-3.40(±0.012)

0.05	-3.35(±0.012)	-3.36(±0.012)	-3.37(±0.012)	-3.39(±0.012)
		N-Acetyl L-Cysteine		
		$V_\phi^0 \times 10^6$ / (m^3·mol^{-1})		
0.000	118.53(±0.008) 118.53 [31]	119.69(±0.007) 119.69 [31]	120.93(±0.007) 120.93 [31]	122.40(±0.007) 122.45 [31]
0.005	118.61(±0.008)	119.72(±0.007)	120.96(±0.007)	122.44(±0.007)
0.01	118.67(±0.008)	119.79(±0.007)	121.05(±0.007)	122.57(±0.007)
0.03	118.82(±0.008)	119.88(±0.007)	121.13(±0.007)	122.61(±0.007)
0.05	119.05(±0.008)	120.01(±0.007)	121.26(±0.007)	122.69(±0.008)
		$S_v \times 10^6$ / (m^3·kg·mol^{-2})		
0.000	-5.12(±0.017)	-5.07(±0.017)	-5.02(±0.016)	-4.97(±0.016)
0.005	-5.11(±0.017)	-5.06(±0.017)	-5.02(±0.016)	-4.97(±0.016)
0.01	-5.10(±0.017)	-5.05(±0.017)	-5.01(±0.016)	-4.95(±0.016)
0.03	-5.08(±0.017)	-5.04(±0.017)	-4.99(±0.016)	-4.94(±0.016)
0.05	-5.05(±0.017)	-5.01(±0.016)	-4.97(±0.016)	-4.92(±0.015)

[a] m_B is the molality of aqueous 1-hexyl-3-methylimidazolium bromide solutions.

Table 4

Values of empirical parameters of equation (4) of L-cysteine and N-acetyl L-cysteine in aqueous solution of 1-hexyl-3-methylimidazolium bromide along with average relative deviation (ARD) values

[a]m_B / (mol·kg^{-1})	$a \times 10^6$ / (m^3·mol^{-1})	$b \times 10^6$ /(m^3·mol^{-1}·K^{-1})	$c \times 10^6$/(m^3·mol^{-1}·K^{-2})	ARD(σ)
		L-Cysteine		
0.000	74.02	0.0053	-0.00001	0.0001
0.005	74.05	0.0049	0.00011	0.0005
0.01	74.09	0.0053	0.00009	0.0006
0.03	74.17	0.0049	0.00012	0.0005
0.05	74.25	0.0096	0.00001	0.0003
		N-Acetyl L-cysteine		
0.000	119.67	0.1206	0.00078	0.0005
0.005	119.71	0.1181	0.00091	0.0003
0.01	119.77	0.1195	0.00100	0.0005
0.03	119.87	0.1155	0.00100	0.0002
0.05	120.03	0.1099	0.00118	0.0003

[a]m_B is the molality of aqueous 1-hexyl-3-methylimidazolium bromide solutions

Table 5

Values of speed of sound c and apparent molar isentropic compression ($K_{\phi,s}$) of L-cysteine and N-acetyl L-cysteine in aqueous solutions of 1-hexyl-3-methylimidazolium bromide at different temperatures and experimental pressure p = 0.1 MPa.

$^{a}m_A$	c/ (m·s^{-1})				$K_{\phi,S} \times 10^6$/(m^3.·mol^{-1}.GPa^{-1})			
/(mol·kg^{-1})	T=288.15 K	T=298.15 K	T=308.15 K	T=318.15 K	T=288.15 K	T=298.15 K	T=308.15 K	T=318.15 K
				L-Cysteine + 0.00 mol·kg^{-1} [C$_6$mim][Br]				
0.00000	1466.73	1495.87	1519.50	1536.30				
0.09925	1474.37	1502.98	1526.01	1542.75	-46.24	-44.46	-43.08	-42.14
0.19669	1481.88	1509.95	1532.41	1549.06	-46.69	-44.89	-43.50	-42.55
0.29859	1489.72	1517.25	1539.10	1555.71	-46.99	-45.18	-43.79	-42.84
0.40044	1497.56	1524.54	1545.78	1562.33	-47.26	-45.43	-44.03	-43.08
0.49783	1505.06	1531.51	1552.17	1568.66	-47.49	-45.66	-44.26	-43.30
0.59624	1512.64	1538.56	1558.63	1575.06	-47.72	-45.88	-44.47	-43.51
0.69817	1520.49	1545.86	1565.32	1581.68	-47.96	-46.11	-44.69	-43.73
				L-Cysteine + 0.005 mol·kg^{-1} [C$_6$mim][Br]				
0.00000	1467.09	1496.69	1520.25	1536.59				
0.09953	1475.16	1504.25	1526.76	1542.62	-46.22	-44.41	-43.04	-42.13
0.20096	1483.38	1511.95	1533.39	1548.77	-46.68	-44.85	-43.47	-42.55
0.30044	1491.45	1519.51	1539.90	1554.81	-46.97	-45.13	-43.75	-42.82

0.39702	1499.28	1526.84	1546.22	1560.66	-47.22	-45.37	-43.98	-43.05
0.50209	1507.80	1534.82	1553.09	1567.03	-47.48	-45.62	-44.22	-43.29
0.59963	1515.71	1542.23	1559.47	1572.95	-47.71	-45.84	-44.43	-43.50
0.69078	1523.10	1549.15	1565.43	1578.47	-47.93	-46.04	-44.63	-43.71
L-Cysteine + 0.01 mol·kg^{-1} [C_6mim][Br]								
0.00000	1467.79	1497.39	1521.13	1537.07				
0.09778	1476.11	1505.21	1527.62	1543.19	-46.17	-44.36	-42.98	-42.09
0.19770	1484.61	1513.20	1534.26	1549.45	-46.62	-44.80	-43.41	-42.51
0.29943	1493.27	1521.33	1541.01	1555.82	-46.93	-45.09	-43.69	-42.79
0.40108	1501.91	1529.46	1547.76	1562.19	-47.19	-45.34	-43.94	-43.03
0.50207	1510.51	1537.53	1554.47	1568.51	-47.43	-45.58	-44.17	-43.26
0.59443	1518.36	1544.91	1560.60	1574.30	-47.65	-45.78	-44.37	-43.46
0.70079	1527.41	1553.42	1567.67	1580.96	-47.89	-46.02	-44.60	-43.68
L-Cysteine + 0.03 mol·kg^{-1} [C_6mim][Br]								
0.00000	1470.95	1500.43	1523.15	1538.97				
0.10096	1479.54	1508.50	1529.85	1545.29	-45.99	-44.20	-42.89	-42.01
0.19737	1487.75	1516.21	1536.26	1551.33	-46.42	-44.61	-43.29	-42.41
0.30194	1496.64	1524.57	1543.20	1557.88	-46.73	-44.91	-43.58	-42.69
0.40114	1505.08	1532.50	1549.79	1564.09	-46.98	-45.16	-43.82	-42.93
0.51424	1514.70	1541.54	1557.30	1571.18	-47.25	-45.42	-44.07	-43.18

0.60874	1522.74	1549.10	1563.57	1577.10	-47.47	-45.63	-44.28	-43.38
0.69922	1530.44	1556.33	1569.58	1582.76	-47.68	-45.83	-44.47	-43.57
L-Cysteine + 0.05 mol·kg^{-1} [C_6mim][Br]								
0.00000	1474.12	1503.46	1525.26	1540.88				
0.09959	1482.59	1511.43	1531.87	1547.12	-45.78	-44.01	-42.76	-41.89
0.19667	1490.85	1519.19	1538.32	1553.20	-46.22	-44.43	-43.17	-42.30
0.30020	1499.66	1527.46	1545.19	1559.68	-46.52	-44.72	-43.46	-42.58
0.40158	1508.28	1535.57	1551.93	1566.03	-46.78	-44.97	-43.70	-42.82
0.50010	1516.66	1543.45	1558.47	1572.20	-47.02	-45.20	-43.92	-43.03
0.59788	1524.98	1551.26	1564.96	1578.33	-47.24	-45.42	-44.13	-43.24
0.69436	1533.19	1558.98	1571.37	1584.37	-47.46	-45.63	-44.33	-43.45
N-Acetyl L-Cysteine + 0.00 mol·kg^{-1} [C_6mim][Br]								
0.00000	1466.73	1495.87	1519.50	1536.12				
0.09801	1472.81	1500.64	1523.62	1540.05	-46.22	-44.43	-43.05	-42.12
0.20405	1479.38	1506.23	1528.08	1544.29	-46.69	-44.88	-43.48	-42.54
0.29892	1485.26	1511.04	1532.06	1548.09	-46.96	-45.13	-43.73	-42.77
0.39788	1491.40	1516.06	1536.22	1552.06	-47.20	-45.36	-43.95	-42.98
0.50464	1498.02	1521.48	1540.71	1556.33	-47.45	-45.60	-44.17	-43.20
0.59896	1503.87	1526.27	1544.67	1560.11	-47.66	-45.79	-44.36	-43.38
0.69517	1509.83	1531.15	1548.72	1563.97	-47.87	-45.99	-44.55	-43.56

N-Acetyl L-Cysteine + 0.005 mol·kg^{-1} [C_6mim][Br]

0.00000	1467.09	1496.62	1520.25	1536.59				
0.09902	1473.61	1501.97	1524.46	1540.13	-46.20	-44.39	-43.02	-42.10
0.19827	1480.15	1507.33	1528.68	1543.67	-46.65	-44.81	-43.42	-42.49
0.29648	1486.62	1512.64	1532.86	1547.18	-46.93	-45.08	-43.68	-42.74
0.39760	1493.29	1518.11	1537.16	1550.80	-47.18	-45.32	-43.90	-42.96
0.49470	1499.68	1523.35	1541.29	1554.27	-47.40	-45.53	-44.10	-43.15
0.59780	1506.48	1528.93	1545.68	1557.95	-47.63	-45.75	-44.31	-43.35
0.69278	1512.73	1534.06	1549.72	1561.34	-47.84	-45.94	-44.50	-43.53

N-Acetyl L-Cysteine + 0.01 mol·kg^{-1} [C_6mim][Br]

0.00000	1467.79	1497.38	1521.13	1537.07				
0.10118	1474.59	1502.85	1525.43	1540.71	-46.17	-44.36	-42.98	-42.08
0.19957	1481.20	1508.16	1529.62	1544.24	-46.60	-44.77	-43.37	-42.47
0.29819	1487.82	1513.49	1533.81	1547.78	-46.88	-45.04	-43.63	-42.71
0.40024	1494.68	1519.01	1538.15	1551.45	-47.14	-45.27	-43.86	-42.93
0.49565	1501.09	1524.17	1542.21	1554.88	-47.35	-45.48	-44.05	-43.12
0.59806	1507.97	1529.70	1546.57	1558.56	-47.58	-45.70	-44.26	-43.32
0.69937	1514.78	1535.17	1550.88	1562.20	-47.80	-45.90	-44.45	-43.51

N-Acetyl L-Cysteine + 0.03 mol·kg^{-1} [C_6mim][Br]

0.00000	1470.95	1500.42	1523.15	1538.97				

0.10082	1477.72	1505.87	1527.44	1542.53	-45.97	-44.18	-42.86	-41.98
0.19808	1484.26	1511.12	1531.58	1545.95	-46.40	-44.58	-43.25	-42.36
0.29747	1490.94	1516.50	1535.80	1549.46	-46.68	-44.85	-43.51	-42.61
0.39883	1497.74	1521.97	1540.11	1553.03	-46.93	-45.08	-43.73	-42.82
0.49476	1504.19	1527.16	1544.19	1556.42	-47.14	-45.29	-43.93	-43.01
0.60365	1511.50	1533.04	1548.83	1560.26	-47.38	-45.52	-44.15	-43.22
0.69732	1517.80	1538.10	1552.81	1563.56	-47.59	-45.71	-44.33	-43.39
N-Acetyl L-Cysteine + 0.05 mol·kg^{-1} [C$_6$mim][Br]								
0.00000	1474.11	1503.46	1525.26	1540.88				
0.10167	1480.94	1508.95	1529.58	1544.44	-45.78	-44.01	-42.75	-41.88
0.20044	1487.58	1514.29	1533.79	1547.91	-46.20	-44.41	-43.14	-42.26
0.29805	1494.13	1519.57	1537.94	1551.33	-46.48	-44.67	-43.39	-42.50
0.40630	1501.41	1525.42	1542.54	1555.13	-46.74	-44.91	-43.62	-42.73
0.50017	1507.71	1530.49	1546.53	1558.42	-46.95	-45.11	-43.81	-42.91
0.59864	1514.33	1535.81	1550.72	1561.87	-47.16	-45.32	-44.01	-43.10
0.69941	1521.10	1541.26	1555.01	1565.40	-47.38	-45.52	-44.20	-43.28

[a] m_A is the molality of amino acids in aqueous 1-hexyl-3-methylimidazolium bromide solutions. Standard uncertainties u are $u(c)$ = 0.05 m·s^{-1}; $u(m) = 2 \times 10^{-5}$ mol·kg^{-1}; $u(T)$ = 0.001 K and u (p) = 0.01 MPa

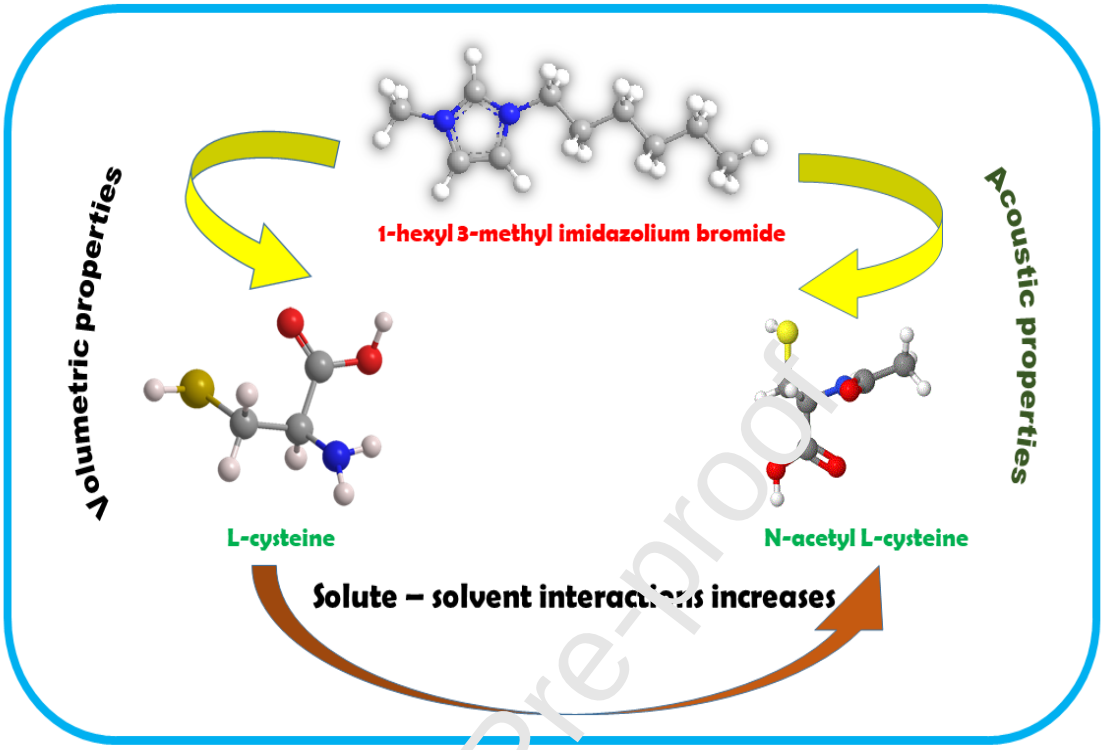
Table 6

Apparent molar isentropic compression, $K^0_{\phi,s}$ and experimental slopes, S^*_K of L-cysteine and N-acetyl L-cysteine in aqueous solutions of 1-hexyl-3-methylimidazolium bromide at different temperatures.

$^{a}m_B$ / (mol·kg^{-1})	288.15 K	298.15 K	308.15 K	318.15 K
		L-Cysteine		
		$K^0_{\phi,s} \times 10^6$ / (m^3·mol^{-1}·GPa^{-1})		
0.000	-46.09(±0.067)	-44.31(±0.065)	-42.94(±0.063)	-42.01(±0.062)
0.005	-46.07(±0.065)	-44.29(±0.065)	-42.90(±0.063)	-41.99(±0.060)
0.01	-46.02(±0.068)	-44.22(±0.066)	-42.85(±0.064)	-41.96(±0.063)
0.03	-45.84(±0.065)	-44.05(±0.062)	-42.74(±0.061)	-41.87(±0.060)
0.05	-45.63(±0.065)	-43.87(±0.063)	-42.62(±0.062)	-41.76(±0.061)
		$S^*_K \times 10^6$ / (kg·m^3·mol^{-2}·GPa^{-1})		
0.000	-2.76(±0.151)	-2.66(±0.146)	-2.59(±0.142)	-2.55(±0.140)
0.005	-2.77(±0.147)	-2.66(±0.146)	-2.59(±0.142)	-2.56(±0.135)
0.01	-2.76(±0.154)	-2.66(±0.148)	-2.59(±0.145)	-2.55(±0.143)

0.03	-2.72(±0.144)	-2.62(±0.139)	-2.55(±0.135)	-2.51(±0.134)
0.05	-2.72(±0.148)	-2.62(±0.142)	-2.55(±0.139)	-2.51(±0.138)
		N-Acetyl L-Cysteine		
		$K^0_{\phi,s} \times 10^6$ / ($m^3 \cdot mol^{-1} \cdot GPa^{-1}$)		
0.000	-46.09(±0.069)	-44.31(±0.067)	-42.94(±0.065)	-42.01(±0.064)
0.005	-46.07(±0.067)	-44.27(±0.065)	-42.90(±0.063)	-41.99(±0.062)
0.01	-46.03(±0.065)	-44.23(±0.063)	-42.85(±0.061)	-41.97(±0.061)
0.03	-45.83(±0.065)	-44.05(±0.063)	-42.74(±0.061)	-41.86(±0.060)
0.05	-45.64(±0.064)	-43.87(±0.062)	-42.62(±0.060)	-41.76(±0.060)
		$S^*_K \times 10^6$ / ($kg \cdot m^3 \cdot mol^{-2} \cdot GPa^{-1}$)		
0.000	-2.65(±0.153)	-2.51(±0.150)	-2.40(±0.146)	-2.31(±0.144)
0.005	-2.64(±0.152)	-2.50(±0.147)	-2.39(±0.143)	-2.30(±0.141)
0.01	-2.62(±0.147)	-2.48(±0.142)	-2.37(±0.138)	-2.28(±0.136)
0.03	-2.60(±0.146)	-2.36(±0.141)	-2.27(±0.138)	-2.27(±0.136)
0.05	-2.57(±0.143)	-2.44(±0.138)	-2.34(±0.135)	-2.25(±0.134)

[a] m_B is the molality of aqueous 1-hexyl-3-methylimidazolium bromide solutions.



Scheme 1

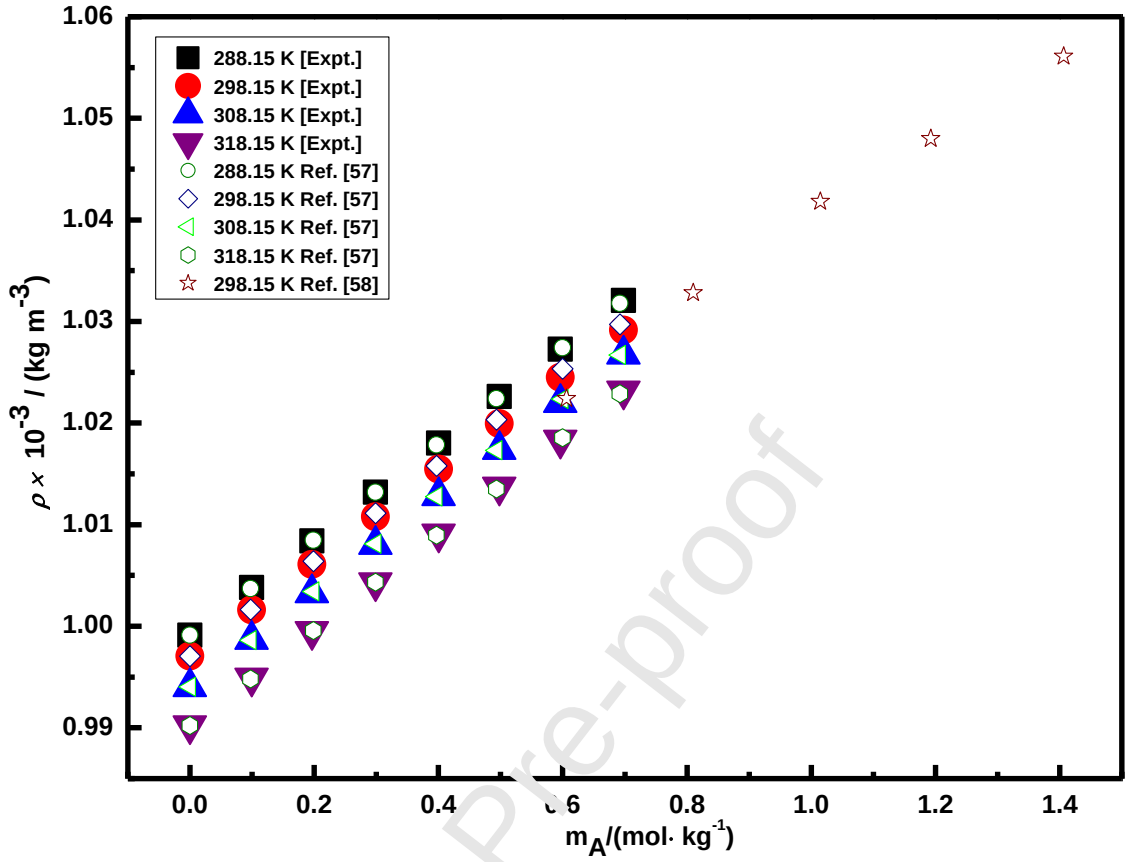


Figure 1

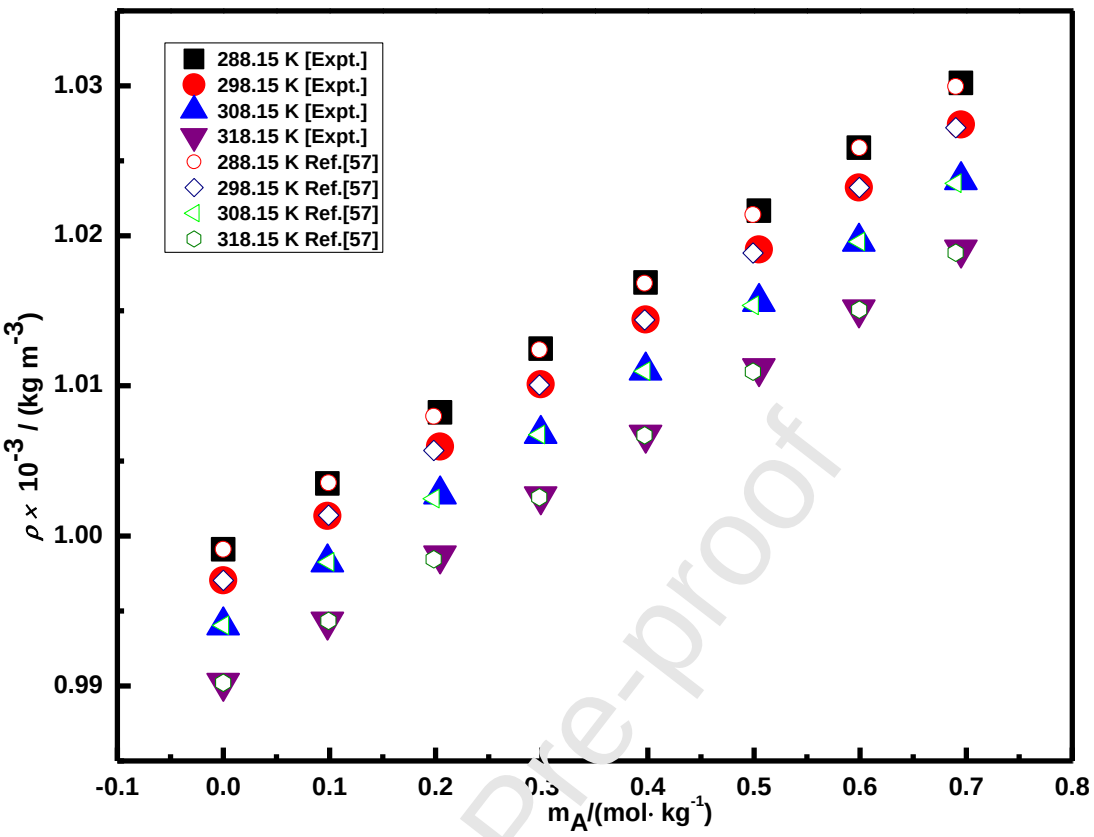
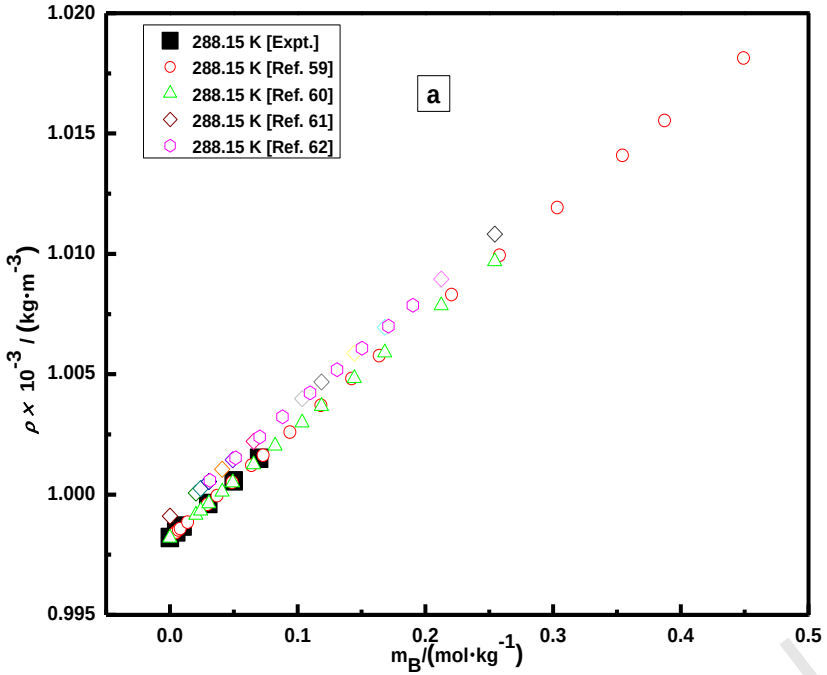
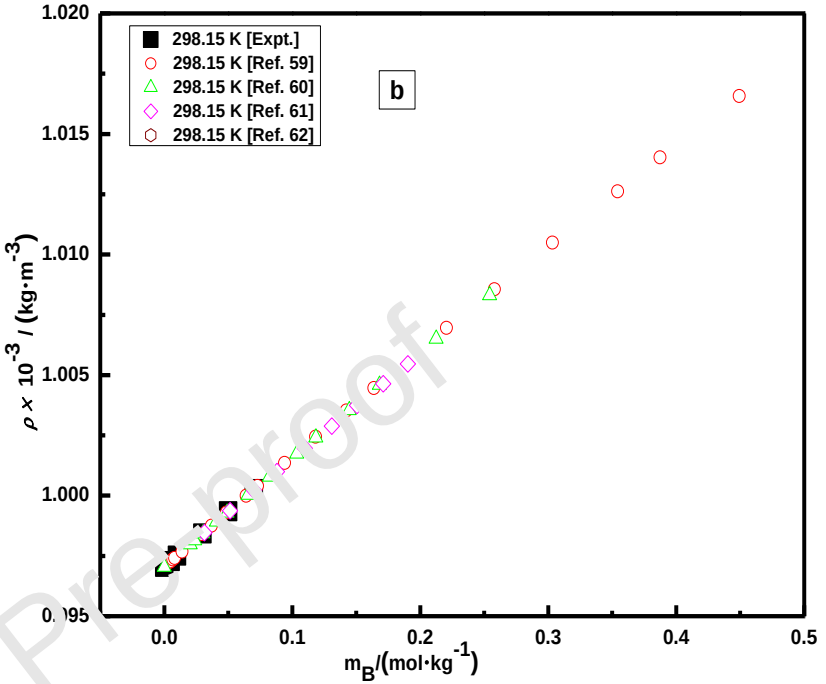


Figure 2





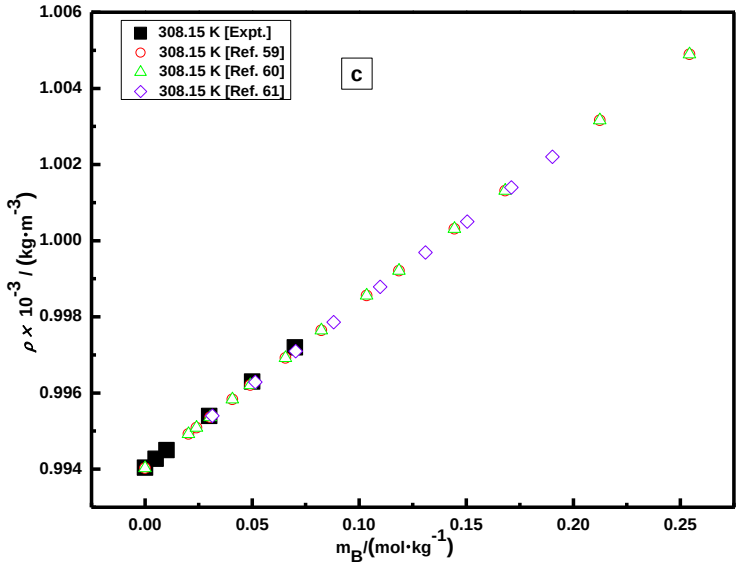


Figure 3

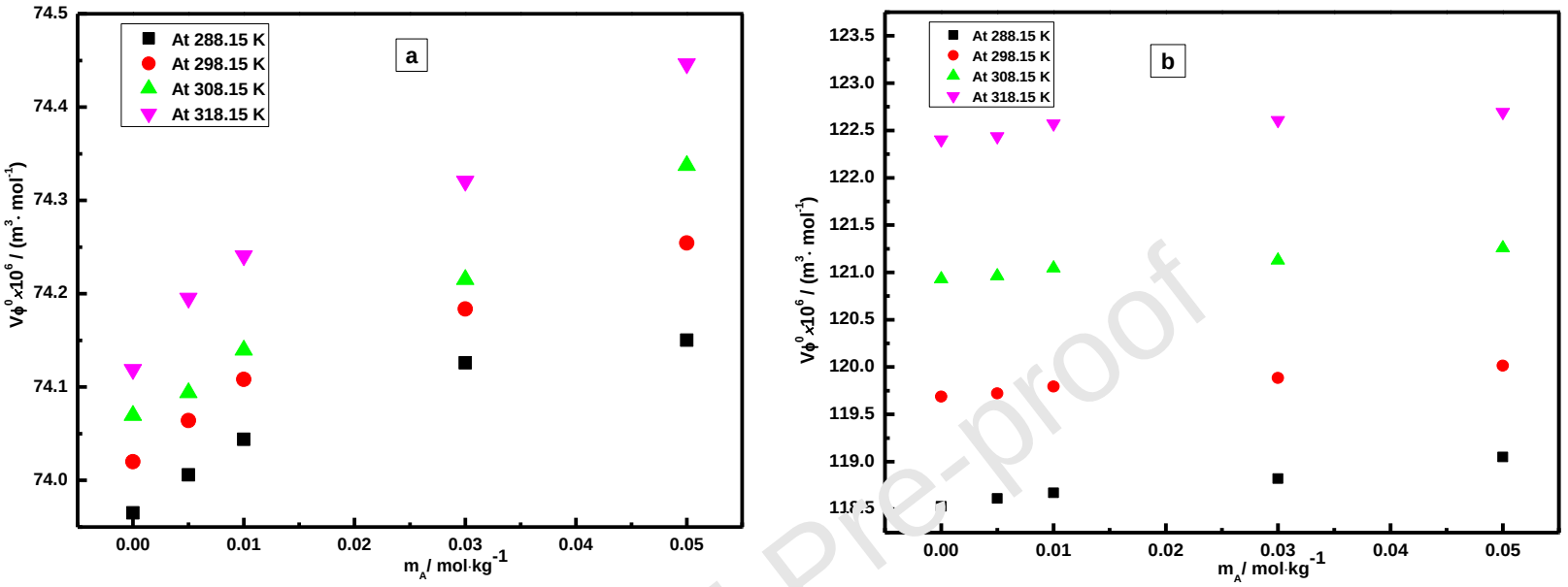


Figure 4

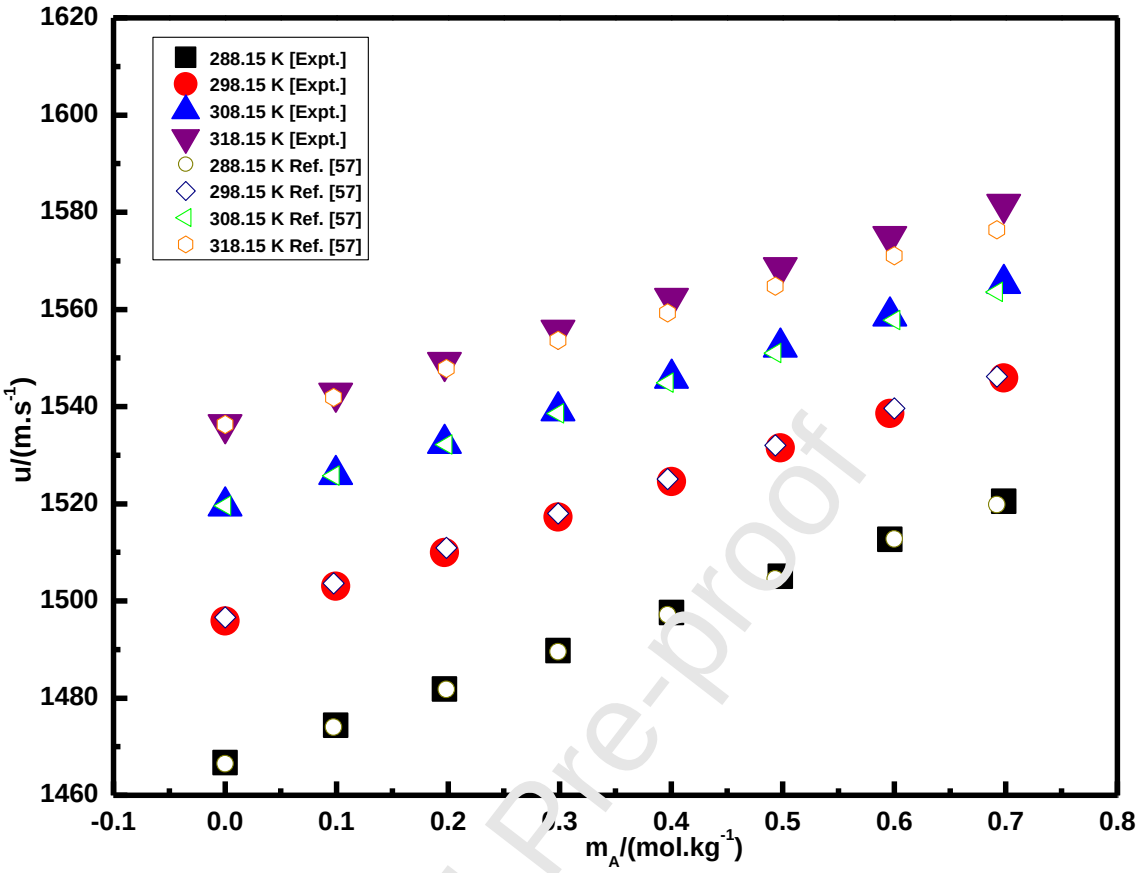


Figure 5

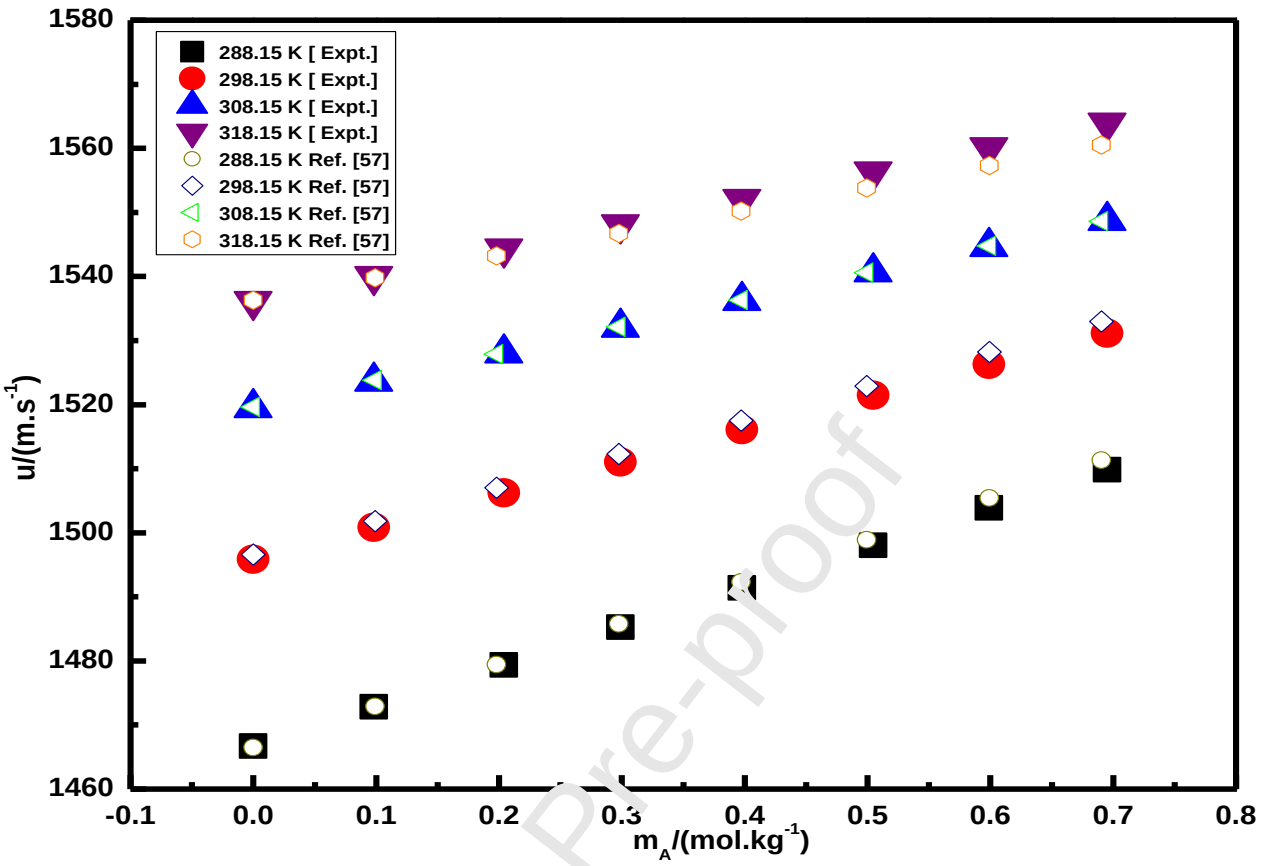
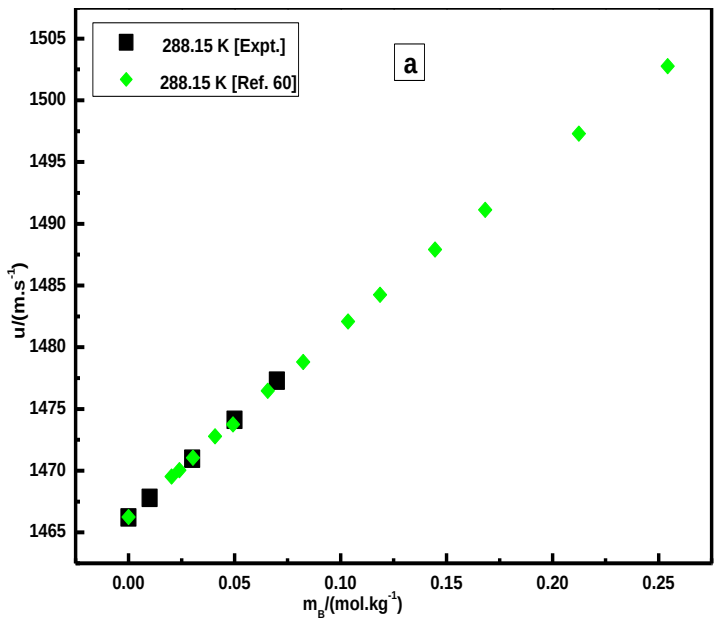
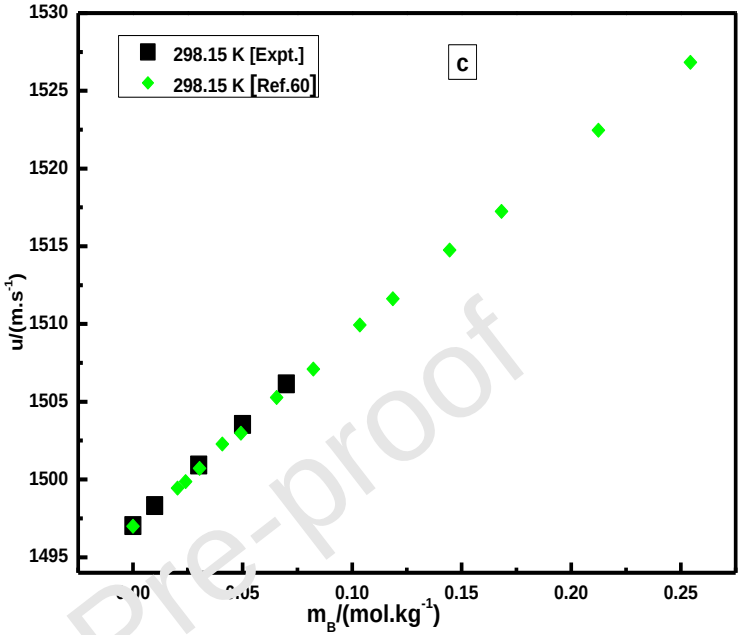


Figure 6





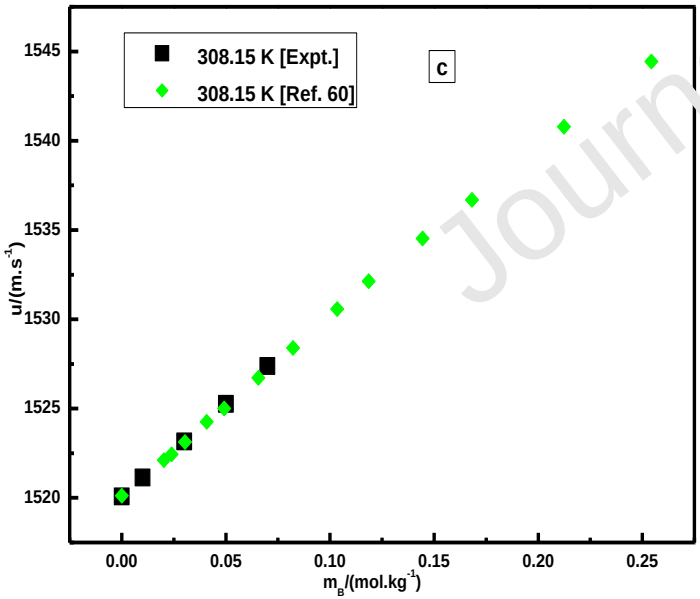


Figure 7

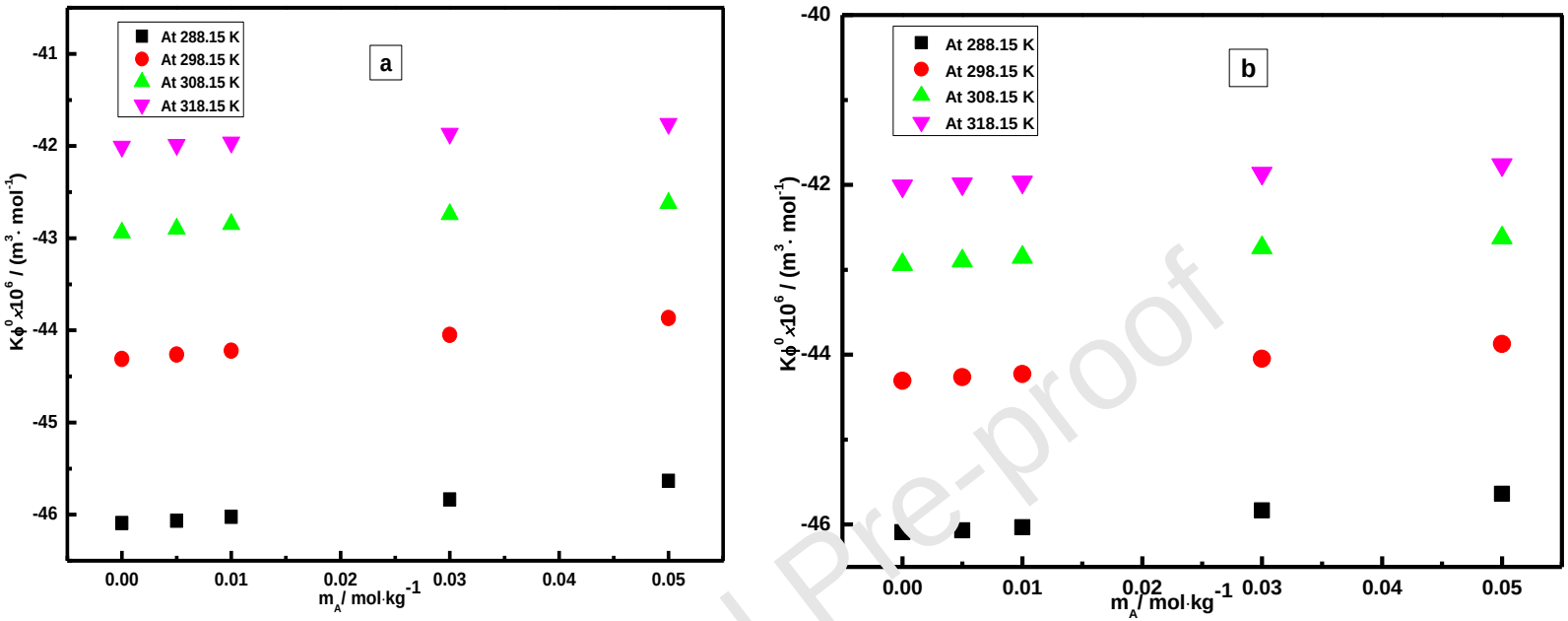


Figure 8

Exploration of the solvation behavior of the synthesized 1-hexyl-3-methylimidazolium bromide [C_6mim][Br] ionic liquid with L-cysteine and N-acetyl L-cysteine) in aqueous medium at different temperatures

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Research Highlights

New data on density and speeds of sound for L-cysteine and N-acetyl L-cysteine in aqueous [C_6mim][Br] solutions

Apparent molar volume properties shows the dominance of (solute + solvent) interactions.

Transfer parameters predict the ion hydrophilic interactions.

Structure making ability of amino acids in aqueous ionic liquid solutions

Pair wise interactions are predicted in (amino acids + water + ionic liquid) mixtures