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Synthesis and thermodynamics studies of ionic liquid 1-methyl-3-pentylimidazolium bromide ([C_5mim][Br]) with amino acids (L-cysteine and N-acetyl-L-cysteine) at different temperatures

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ABSTRACT

Ionic liquid 1-methyl-3-pentylimidazolium bromide have been synthesised and confirmed by characterisation techniques H^1 NMR, C^{13} NMR, MASS and IR spectroscopy. Density and speed of sound of aqueous amino acids (L-cysteine and N-acetyl-L-cysteine) in aqueous ionic liquid (0.005, 0.01, 0.03, 0.05) mol·kg^{-1} as solvent have been determined at four different temperatures T = (288.15, 298.15, 308.15, 318.15) K. Using these experimental data apparent molar volumes (V_ϕ), limiting apparent molar volume (V_ϕ°), experimental slope (S_v), standard partial molar volumes of transfer ($\Delta V_\phi{}^0$), Limiting apparent molar expansibilities (E_ϕ°), apparent molar isentropic compression ($K_{\phi,s}$), limiting apparent molar isentropic compression ($\kappa^0_{\phi,s}$) and standard partial molar isentropic compression of transfer ($\Delta\kappa^0_{\phi,s}$) have been evaluated. The pair and triplet interaction coefficient have also been calculated. The values of these parameters are helpful for interpretation in terms of solute-solute and solute-solvent interactions, ion hydrophilic, hydrophilic–hydrophilic and hydrophilic–hydrophobic interactions in the amino acid and ionic liquid solutions. The structure making or structure-breaking tendency of amino acids has also been studied using these thermodynamic parameters.

1. Introduction

For better understanding of molecular interaction with in biologically important structures, the knowledge about thermodynamic properties is a necessity. The solute-solvent and solute-solute interactions in solutions are studied by thermodynamic and physicochemical measurements [1–5].The protein molecules are held in 3-D structures and attain stability via intra and intermolecular interactions. The specific biological activities of proteins are the result of their structure. These interactions, hence protein stability is greatly influenced by change in their surrounding environment as a result the structure and configuration of protein are greatly affected [6] this is important to have required knowledge about molecular interactions between protein structure and groups surrounding them [7]. Volumetric studies [8–14] are quite valuable for required information on folding/unfolding behaviour and conformational stability of protein [15,16]. Since protein molecule attain complex configuration and confirmation, their direct study is quite difficult. Hence their basic units *i.e.* amino acids are studied. Amino acids are bioactive organic compounds containing amine and carboxylic acid group with side chains and are found in all living organism on earth. They have large biological and industrial importance and are applicable for variety of applications especially in food, chemical, medical, pharmaceutical, and cosmetics industries. The interactions of water with the various functional groups of amino acids play a crucial role for determining the proteins conformational stability [17]. Salt-protein interaction induced electrostatic forces are used for modifying the protein structure as the properties like solubility, activity of enzymes and denaturation are accomplished [7].

Ionic liquids are salts consisting pure ions generally bulky organic cation and organic or inorganic anion. They are widely used as novel medium for bimolecular processes so these solutions are topic of research from last few decades [18,19]. In aqueous solutions ionic liquids as additives show unique effects different from normal salts or standard buffers for many bioprocesses [20–22]. The study of phase equilibrium and thermophysical properties of solution containing aqueous ionic liquids and individual small molecules are useful to understand different interactions taking place within aqueous ionic liquid solutions and giant macromolecules [23–26]

Although there are studies of ionic liquids with variety of additives [27–34], many studies have already been carried out on amino

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acids with traditional salts but yet ionic liquids and amino acid mixtures have not been studied that much. Studying volumetric and acoustical properties of aqueous ionic liquid-amino acid solutions gives information about interactions, association and solvation behaviour. As an effort to get more information about these mixtures, we have carried out volumetric and acoustic studies for mixtures containing amino acids (L-cysteine and N-acetyl-L-cysteine) with aqueous ionic liquid 1-methyl-3-pentylimidazolium bromide ([C_5mim][Br]) at different temperatures. Densities and speeds of sound have been measured for these solutions and the effect of temperature and concentration has been studied. As per our knowledge no studies on densities and speeds of sound of these amino acids with 1-pentyl-3-methylimidazolium bromide have been reported yet. Using these results thermodynamic parameters has been calculated and solute-solute and solute-solvent interactions present in solution are discussed.

2. Experimental

2.1. Materials

1-Methyl imidazole (Acros Organics, USA with mass fraction purity 0.99), 1-bromopentane (Acros Organics, USA with mass fraction purity 0.98), acetonitrile HPLC grade (SD Fine Chem Ltd. with mass fraction purity 0.998) and ethyl acetate HPLC grade (SD Fine Chem Ltd. with mass fraction purity >0.99) were used for the synthesis of ionic liquid 1-pentyl-3-methylimidazolium bromide [C_5mim][Br]. These reagents were used without further purification. L-cysteine and N-acetyl-L-cysteine with mass purification purities ≥0.99 were obtained from Merck, Germany. These were dried and stored in vacuum desiccators over P_2O_5 for at least two days before their use. The details and specifications of the chemicals are given in Table 1.

2.2. Apparatus and procedures

Freshly prepared triple distilled and degassed water (specific conductance $<10^{-6}$ S·cm^{-1}) was used for the preparation of solutions. The solutions were prepared by weighing on a Sartorius CPA 225 D balance having a precision of ±0.00001 g. The relative uncertainties in the molality as per purities of the chemicals are $u_r(m_A) = 1\%$ and $u_r(m_{[C5mim][Br]}) = 1\%$, respectively.

For the synthesis of ionic liquid, 1-methyl-3-pentylimidazolium bromide, [C_5mim][Br], a mixture of fresh and distilled 1-methylimidazole and 1-bromopentane in a ratio 1:1.1 (14.56 ml of 1-methyl-3-pentylimidazolium and 25.087 mL of bromopentane) in acetonitrile was reacted in a round bottom flask of 500 mL at $T = 353$ K using oil bath for 3 days under water condenser. Extend of reaction was checked with the help of TLC. Non-reacted 1-bromopentane was decanted from the reaction mixture. In an additional extraction step, the ionic liquid was extracted three times with ethyl acetate. The product was dried in high vacuum using a rotary evaporator at reduced pressure.

The ^{1}H and ^{13}C NMR spectra of synthesised IL were recorded on Brüker Ascend 500 spectrometer (AVANCE III HD console). All the measurements were recorded using $CDCl_3$ as solvent using tetramethylsilane (TMS) as an external standard. The mass spectrum of synthesised IL was recorded using Water Q-ToF micro mass equipment with ESI as ion source. Its effect on ion formation was recorded. The FT-IR spectrum of IL was recorded using Agilent Cary 630 FT-IR. For sampling, a drop of sample was placed on the trough for collecting data.

Density and speeds of sound measurements were made on Anton Paar DSA 5000M densimeter simultaneously. The speeds of sound are 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 [35]. Thus, the speeds of sound are obtained by dividing the known distance between transmitter and receiver by the measured propagation time of the sound wave. Before each series of measurements, the densimeter was calibrated with triple distilled and degassed water, in the experimental temperature range. The density and speeds of sound values are extremely sensitive to temperature, so it was controlled to $\pm 1 \times 10^{-3}$ K by a built-in Peltier device. The sensitivity of the instrument corresponds to a precision in density and speeds of sound measurements of 1×10^{-3} kg·m^{-3} and 1×10^{-2} m·s^{-1}. The standard uncertainty of the density and speeds of sound estimates was found to be within ±0.15 kg·m^{-3} and ±0.5 m·s^{-1}, respectively.

3. Results and discussion

3.1. Synthesis of the ionic liquid [C5mim][Br]

The desired ionic liquid *i.e.* 1-methyl-3-pentylimidazolium bromide [C_5mim][Br] was synthesised successfully and analysed with the help of Mass, ^{1}H NMR, FT-IR and ^{13}C NMR spectra to confirm the absence of any major impurities and they were found to be in good agreement with those reported in the literature [36]. The mass, ^{1}H NMR, FTIR and ^{13}C spectra are given in Figs. 1–4. There are three extra peaks in the ^{1}H NMR spectrum. These are: (i) peak at 7.26×10^{-6} is of $CHCl_3$ as the spectra is recorded in $CDCl_3$; (ii) peak around 2.0×10^{-6} which is not integrated is from traces of water present in ionic liquid and $CDCl_3$ (intensity of the peak show that % of moisture is minimum) and (iii) a very small peak near TMS signal which is taken at reference zero ppm point appears sometimes in the deuterated solvents containing TMS. The peak integrals for all the peaks are within error with the exception of peak around 2×10^{-6}. It is natural that the extra peak due to the

Table 1
Provenance and mass fraction purity of the materials studied.

Chemical	CAS number	Source	Purification method	[a]Mass fraction purity
L-Cysteine	52-90-4	Merck, Germany	Vacuum drying	≥0.99
N-Acetyl-L-Cysteine	616-91-1	Merck, Germany	Vacuum drying	≥0.99
Acetonitrile	78-05-8	SD Fine Chem Ltd., India	Used as such	0.998
1-Methyl imidazole	616-47-7	Acros Organics, USA	Used as such	0.99
1-Bromopentane	110-53-2	Acros Organics, USA	Used as such	0.98
Ethyl acetate	141-78-6	SD Fine Chem Ltd., India	Used as such	>0.99
1-methyl-3-pentylimidazolium bromide [C_5mim][Br]	343851-31-0	Synthesised in the laboratory	Vacuum drying	>0.98 (on the basis of spectroscopic analysis)

[a] As declared by supplier.