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Hydration properties of glycylglycine in aqueous ionic liquid solutions at different temperatures: Volumetric and acoustic approach

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ABSTRACT

The apparent molar volume and isentropic compression of glycylglycine in aqueous 1-methylimidazolium chloride, [mim][Cl], 1-ethyl-3-methylimidazolium chloride [C_2mim][Cl], and 1-methyl-3-octylimidazolium chloride [C_8mim][Cl] solutions have been calculated from the measured experimental data on density and speed of sound at temperature, $T = 288.15$, 298.15 and 308.15 K. The apparent molar volumes at infinite dilution, V_ϕ^0 and the apparent isentropic molar compression at infinite dilution $K_{\phi,S}^0$, were also calculated. Furthermore, apparent specific volumes, apparent molar expansivity, E_ϕ^0, Hepler's constant values, $\left(\frac{\partial E_\phi^0}{\partial T}\right)_P$ and hydration numbers, n_H, have been evaluated to support the conclusions obtained from the volumetric and acoustic studies. The Hepler's constant values were found negative which indicating the peptide under study is predominantly a structure breaker due to hydrophobic hydration of small peptide in aqueous ionic liquid.

1. Introduction

Room temperature ionic liquids are blessed with an array of physicochemical properties like high thermal stability, high electrical conductivity, negligible vapor pressure, low nucleophilicity and excellent solvation ability [1–4]. In past decades, the research in the field of room temperature ionic liquid has spotted a prodigious growth. Some of 1-alkyl-3-methylimidazolium salts can also exhibit the surfactant-like behavior as they have been found to form micellar aggregates in aqueous solutions [5,6].

Amino acids and peptides are the building blocks of proteins and dipeptides with significant biological and industrial importance. These biomolecules are widely used in many applications, mainly, in the pharmaceutical, food and chemical industries. The direct study of proteins is strenuous due to their complex configurational and conformational aspects in aqueous solution [7]. Therefore, the systematic study of interactions between ionic liquids and small peptide can also provide valuable information about dipeptide's behavior and insight into the conformational stability of proteins in ionic liquid solutions [8,9].

There have been some reports in the literature on interactions of small biomolecules like amino acids and monosaccharaides with ionic liquids but limited study has been done on the interactions of ionic liquids with small peptides [10–15]. In our earlier studies [16,17], it has been observed that both the ionic liquids, 1-butyl-3-methylimidazolium chloride, [C_4mim][Cl] and 1-pentyl-3-methylimidazolium, [C_5mim][Cl] show the presence of strong solute – solvent interaction, which further exert a dehydration effect on peptide. Thus, the understanding of solvation behavior with small peptides in ionic liquid solutions at different temperatures would be more fascinating from practical and academic points of view. Furthermore, such kind of investigations can enlighten the aggregation behavior of ionic liquids in biomolecule mixed systems. These studies would be useful to refine the applications of ionic liquids in industrial and biological systems. The novelty of the present work lies in the fact that there exists no report involving the behavior of glycylglycine at different concentrations of ionic liquids (ILs). This work focused on the behavior of peptide in the presence of different ionic liquids in aqueous solutions, investigated via speed of sound and density measurements.

To fulfil the above objective and in continuation of our previous studies [16,17], we present experimental densities and speeds of sound of glycylglycine in aqueous ionic liquids viz 1-methylimidazolium chloride [mim][Cl], 1-ethyl-3-methylimidazolium chloride [C_2mim][Cl], and 1-methyl-3-octylimidazolium chloride [C_8mim][Cl] at 288.15, 298.15 and 308.15 K. In this study, the ILs having different alkyl chain lengths,C_nH_{2n+1} (n = 0, 2, 8), and same counterions [Cl^-] have been

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considered aiming at a better understanding of the IL cation and anion effects so that some structure – property correlation could be established.

2. Materials and methods

Glycylglycine (Merck-Schuchardt, Germany), GC > 0.99 and 1-methylimidazolium chloride [mim][Cl] GC > 0.95, 1-ethyl-3-methylimidazolium chloride [C_2mim][Cl] GC > 0.98 and 1-methyl-3-octylimidazolium chloride [C_8mim][Cl] with mass fraction > 0.97 (Sigma-Aldrich, USA) have been used in present study. The ionic liquids have been dried overnight at 70 °C and also characterized for purity check using ^{1}H NMR (Bruker 300 MHz) and IR (ABB MB3000). All the aqueous solutions of ionic liquids have been prepared by using triple distilled and degassed water (specific conductance < 10^{-6} S cm^{-1}). The details for investigated chemicals along with their chemical structures have been outlined in Table 1.

All the ternary mixtures were prepared by weighing using an analytical balance (A&D Co. limited electronic balance (Japan, model GR-202)) having a precision of 0.01 mg. All the samples have been prepared into air tight stoppered bottles. The samples were injected into the apparatus immediately after their preparation by using a syringe. The determination of density, ρ and speed of sound, u of the solutions was carried out simultaneously by using digital vibrating-tube density and speed analyzer (DSA 5000 M, Anton Paar, Austria) at $T = 288.15$–308.15 K with 10 K difference and at atmospheric pressure. This equipment has a temperature controller that keeps the samples at working temperature with a stability of ±0.01 K. The instrument was calibrated with double distilled deionized, degassed water, and dry air at atmospheric pressure according to the instructions manual. The uncertainties in the molality of mixture, density and speed of sound are $\pm 10 \times 10^{-5}$ mol kg^{-1}, $\pm 5 \times 10^{-2}$ kg m^{-3} and ± 0.5 m s^{-1}, respectively.

3. Result and discussion

3.1. Volumetric and acoustic properties

The apparent molar volume, V_ϕ, and apparent molar isentropic compression, $K_{\phi,s}$, of glycylglycine in aqueous solution of three ionic liquids (IL); [mim][Cl], [C_2mim][Cl] and [C_8mim][Cl] respectively have been calculated from measured densities, ρ, and speed of sound, u, at $T =$ 288.15, 298.15 and 308.15 K (reported in Table 2), by using the following equations:

$$V_\phi = \frac{M}{\rho} - \frac{(\rho - \rho_0)}{m\rho\rho_0} \quad (1)$$

$$K_{\phi,s} = \frac{(\kappa_s\rho_0 - \kappa_{s,0}\rho)}{m\rho\rho_0} + \frac{\kappa_s M}{\rho} \quad (2)$$

where m and M are molality/mol kg^{-1} of glycylglycine in (IL + water + glycylglycine) mixture and molar mass/kg mol^{-1} of the dissolved solute (glycylglycine). ρ_0, ρ, $\kappa_{s,0}$ and κ_s are the densities/kg m^{-3} and isentropic compression/Pa^{-1} of IL + water and IL + glycylglycine + water, respectively. The calculated values of apparent molar volumes V_ϕ . 10^6/m^3 mol^{-1}, apparent molar isentropic compressions K_ϕ/Pa^{-1} and molal concentration m of glycylglycine in different concentrations of ILs at various temperatures have been reported in Table S1 and depicted graphically in Figs. S1–S3.

The isentropic compression, κ_s values were calculated for the investigated mixtures by using Newton's-Laplace equation:

$$\kappa_s = \frac{1}{u^2\rho} \quad (3)$$

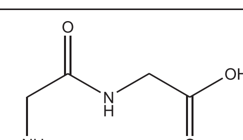
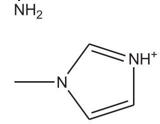
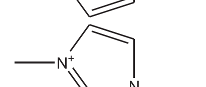
The limiting apparent molar volume, V_ϕ^0, and limiting apparent molar isentropic compression, $K_{\phi,S}^0$, of glycylglycine in the presence of different concentrations of ILs have been obtained by least-square fitting to the following equations:

$$V_\phi = V_\phi^0 + S_v m \quad (4)$$

$$K_\phi = K_{\phi,S}^0 + S_k m \quad (5)$$

In these equations S_v and S_k are the limiting experimental slope also considered as virial pairwise interaction coefficients provide an essential information regarding nature of solute –solute interaction and the apparent molar volume at infinite dilution, V_ϕ^0, (same as standard partial molar volume) and apparent molar isentropic compression at infinite dilution, $K_{\phi,S}^0$, (standard partial molar isentropic compression) reflect the solute-solvent interactions [18]. The values of V_ϕ^0 and $K_{\phi,S}^0$ for (glycylglycine + water) and (glycylglycine + IL + water) systems at

Table 1
A brief summary of the purity of the used chemicals.

Material	Provenance	Mass fraction purity	CAS number	Structure
Glycylglycine	Merck-Schuchardt, Germany	>99%	556-50-3	
1-Methyl-imidazolium chloride	Sigma Aldrich, USA	>95%	35487-17-3	
1-Ethyl-3-methylimidazolium chloride	Sigma Aldrich, USA	>98%	65039-09-0	
1-Methyl-3-octylimidazolium chloride	Sigma Aldrich, USA	>97%	64697-40-1