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Volumetric properties for glycine and L-serine in aqueous solutions of 1-Ethyl-3-methylimidazolium hydrogen sulfate ([Emim][HSO_4]) at T = (293.15–313.15) K and ambient pressure

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ABSTRACT

By using the volumetric properties, the solute–solvent interactions are studied in the ternary (glycine + 1-Ethyl-3-methylimidazolium hydrogen sulfate [Emim][HSO_4] + water) and (L-serine + 1-Ethyl-3-methylimidazolium hydrogen sulfate [Emim][HSO_4] + water) systems. For this purpose, the apparent molar volumes, V_φ, are calculated from the experimental density data. To obtain limiting apparent molar volumes V_φ^0, the apparent molar volume values are fitted to the Redlich-Mayer type equation. Then the limiting apparent molar volumes of transfer, ΔV_φ^0, for studied amino acids from water to aqueous solutions of ionic liquid (IL) are calculated. The results showed that the ΔV_φ^0 values are negative for both ternary systems at all temperatures. The limiting apparent molar expansibility E_φ^0 values have been obtained from the first derivative of limiting apparent molar volumes with respect to temperature. The values of second derivative of limiting apparent molar volumes respect to temperature show the structure making or breaking ability of glycine and L-serine in studied IL aqueous solutions. The results indicated that glycine and L-serine act as structure maker in studied solutions. McMillan–Mayer theory is used for evaluating the interaction parameters. Also the hydration number, n_H, for both amino acids in ternary solutions has been reported.

1. Introduction

Amino acids are biologically important organic compounds that are included of amine (–NH_2) 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 [1]. The study of these compounds in aqueous surroundings can be interesting and useful to enriching our knowledge about their behavior in liquid state. Also one of the other new compounds that have been widely used in different fields and industry are ionic liquids (ILs). 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 vapor pressure, high thermal stability, large liquid range, high hygroscopic ability and large solubility [2,3]. These compounds play a major role in some fields and processes such as biology, separation, electrochemistry and synthesis. In recent years, ionic liquids are used as additives on separation of amino acids in HPLC [4] and in separate peptides [5]. ILs are also used in aqueous biphasic systems consisted of amino acids, owing to ability of framing the polarities by applying the changes in the cation or anion parts of IL [6,7]. Thermophysical properties of aqueous solutions containing amino acids and ILs give us important information about the intermolecular interactions in these mixtures. For this purpose, recently, Xie et al. [8] reported volumetric properties of some amino acids such as: glycine, L-serine, L-alanine and L-proline in 1-phenylpiperazinium tetrafluoroborate aqueous solutions at T = (288.15–308.15) K. Also Shekaari and Jebali [9–11] studied the densities, electrical conductance and refractive indices of some amino acids such as glycine, L-alanine and L-valine in aqueous solutions of ILs ([Hmim][Br], [Hmim][Cl] and [Pmim][Br]) at T = 298.15 K. Also Singh et al. [12] evaluated volumetric properties of glycine and alanine in aqueous solutions of ammonium based protic ionic liquids. In other work, Fang and Ren [13] reported the effect of 1-Ethyl-3-methylimidazolium Bromide on the volumetric behavior of some aqueous amino acids solutions. Roy et al. [1] determined solvation consequences of some α-amino acids in aqueous solution of IL by physicochemical properties and Zafarani–Moattar and Asadzadeh [14] evaluated the effect of 1-carboxymethyl-3-methylimidazolium chloride, [HOOCMMIM][Cl] on volumetric, acoustic and

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transport behavior of aqueous solutions of L-serine and L-threonine at T = 298.15 K. In continuation of these works, in this research, we measured the densities of ternary (glycine or L-serine + [Emim][HSO_4] + H_2O] systems at different temperatures. By using these data, we calculated apparent molar volumes, limiting apparent molar volumes and limiting apparent molar volume transfer of studied amino acids in water to aqueous solutions of IL, limiting apparent molar expansibility and hydration number. These parameters provide useful information about the nature of solute-solute and solute-solvent interactions in studied ternary mixtures.

2. Experimental

2.1. Material

Glycine and L-serine purchased from the Sigma-Aldrich company with minimum mass fraction purity >0.995. Ionic liquid [Emim][HSO_4] obtained from the Merck company with mass fraction purity >0.98. Table 1 shows the material properties.

2.2. Apparatus and procedures

All solutions were prepared afresh by mass using an analytical balance (Sartorius, CP224S, Germany) with precision (10^{-4} g). All the solutions were kept tightly sealed to minimize absorption of atmospheric moisture. The water content in the ILs was determined using a microprocessor based automatic Karl–Fischer Titrator. The mass fraction of water in [Emim][HSO_4] was w = 0.0017. This water content in the ionic liquid was taken into account during preparation of the aqueous solutions. The amino acids were used after drying in a vacuum oven for 24 h at T = 323.15 K. All samples before injection were degassed by using ultrasound instrument (Hielscher UP100H, Germany). Measurements were performed immediately after preparation of solutions. Double distilled water was used for preparation of solutions.

The density of mixtures was measured using a U-tube densimeter (Anton Paar DMA 4500 Austria). The density is extremely sensitive to temperature, so it was automatically kept constant by instrument with its built-in thermostat within ±0.03 K. All measurements were performed three times (with repeatability of 3×10^{-5} g·cm^{-3}) and the reported results are the relevant averages. The experimental uncertainty of density measurements was $\pm 3 \times 10^{-3}$ g·cm^{-3}. The apparatus was calibrated with double distilled deionized, and degassed water, and dry air at ambient pressure which was 0.087 M Pa.

3. Results and discussion

3.1. Apparent molar volume and partial molar volume at infinite dilution

The density values for the binary systems (glycine + H_2O), (L-serine + H_2O) and ternary systems (glycine + [Emim][HSO_4] + H_2O), (L-serine + [Emim][HSO_4] + H_2O) are measured at T = (293.15–313.15 K) and different concentration of IL,(m_{IL} = 0.05, 0.1, 0.15 mol·kg^{-1}) and reported in Supplementary Tables (S1–S4). Figs. 1 and 2 compare the density values for the (glycine + H_2O) and (L-serine + H_2O) systems in this work with those reported in the literature [15–24]. As can be seen from these figures the agreement is very well between our data and the reported values. The apparent molar volumes calculated from the following equation:

$$V_\varphi = \frac{M}{d} - \frac{(d - d_0)}{m d d_0} \quad (1)$$

where M is the molar mass of the solute, m is the molality of the solute, d_0 and d are the densities of the pure solvent and solution, respectively. The apparent molar volume data for investigated systems are also reported in Supplementary Tables (S1–S4) and graphically are shown in the Figs. 3 and 4. In both ternary systems, (IL + H_2O) act as solvent and amino acid is considered as a solute. The results show that the V_φ values for all studied systems increase with increasing both concentration of amino acid and temperature while decrease with elevating the concentration of [Emim][HSO_4]. The apparent molar volume at infinite dilution V_φ^0, is free from the solute–solute interactions and only depends on the solute–solvent

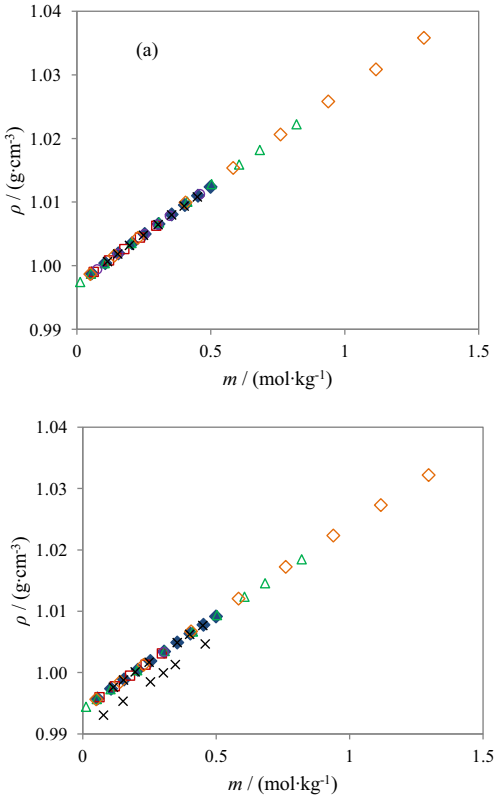

Fig. 1. Density of aqueous glycine solutions plotted against molality of glycine, m, at: (a) T = 298.15 K and (b) T = 308.15 K; ◆, this work; □ [15]; △ [16]; ○ [17]; × [18]; ◇ [19].

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

Compound	CAS	Supplier	Mass fraction purity	Water content as mass fraction[a]	Purity analysis method[b]	Molar mass/(g·mol^{-1})
[Emim][HSO_4]	412009-61-1	Merck	⩾0.98	0.0017	HPLC	208.24
Glycine	56-40-6	Merck	⩾0.995	–	Non	75.07
L-Serine	56-45-1	Merck	⩾0.995	–	Non	105.09

[a] The mass fraction of water in [Emim][HSO_4] are measured by using the Karl–Fischer Titrator.
[b] The Purity Analysis Method reported by supplier and all materials are used without further purification.