Investigation of Volumetric and Acoustic Properties of Ionic Liquid + Amino Acid + Water Systems at Different Temperatures

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This paper reports density and speed of sound data for solutions of the ionic liquids (ILs) [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in aqueous solution of 0.05 w/w amino acids of alanine, serine and proline at T = (288.15, 298.15, 308.15 and 318.15) K. From the experimental data measured, the apparent molar volume (V_ϕ), isentropic compressibility (K$_S$), and apparent molar isentropic compression (K$_\emptyset$) have been calculated. The V_ϕ values of [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in the investigated aqueous amino acid solutions decreased by increasing the hydrophobicity of the amino acid and follow the order: serine > alanine > proline. The apparent molar volume and isentropic compressibility values at infinite dilution of the investigated ILs in the aqueous amino acid solutions and their variations with temperature have been determined. The infinite dilution apparent molar volume and adiabatic compressibility for transfer of the studied ILs from water to aqueous solutions of the amino acids have been calculated and the results were discussed in terms of different interactions existing in these solutions.

Keywords: Ionic liquid, Amino acid, Volumetric, Compressibility, Aqueous solution

INTRODUCTION

Ionic liquids (ILs) are a new class of organic solvents having melting point lower than 373.15 K. These solvents have two green important characteristics: non flammability and negligible vapor pressure [1-2] as well as other interesting physical and chemical properties such as large liquid temperature range, high thermal and chemical stability, excellent ability to dissolve many organic and inorganic solutes and a number of possible variations in cation and anion features that allow the fine-tuning of their properties [3-4]. The literature review shows that the volumetric and acoustic [5-8], vapour pressure osmometery [8-12] and surface tension [13-15] properties of some aqueous solutions of ILs in the absence or presence of the additives such as alcohols [10,16], polymers [17-18], carbohydrates [19-20], electrolytes [8] and amino acids [21-23] have been measured and in some studies, the

respective transfer properties corresponding to change from pure water to aqueous additive media have been obtained. These investigations indicated that interesting interactions are possible in these systems related to the nature of the amino acid side chain and co-solute. One of the interesting and important properties of amino acids is that their aqueous solutions in the presence of a number of ILs can form aqueous biphasic systems (ABS) for which few studies have been reported in the literature [24-26]. IL-amino acid ABS have the additional advantages compared to the conventional polymer-polymer and polymer-salt ABS. However, understanding of the phase splitting mechanism is still incomplete at the molecular level and therefore, studying the various thermodynamic properties of IL-amino acid aqueous solutions is necessary for the better understanding of the driving forces behind the IL-amino acid ABS formation and also improving the extraction efficiencies of these new extraction systems. The evaluation of physicochemical properties of amino acids as basic constituents of proteins can be helpful to achieve procedures

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of purification, separation, and their recovery from natural sources. Measurement of the thermodynamic properties of IL solutions containing amino acids can provide some unique information to extend our knowledge about the interactions between ILs and biological macromolecules [26-27]. To this end, volumetric and compressibility studies of ternary aqueous IL + amino acid solutions provide important information in terms of the molecular interactions between their components. In this work, we study the volumetric and compressibility properties of two imidazolium-based ILs (1-butyl-3-methylimidazolium chloride, [C$_4$mim]Cl and 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate, [C$_4$mim][CF$_3$SO$_3$]) in 0.05 w/w aqueous solutions of three amino acids: l-serine, alanine and l-proline at different temperatures T = (288.15, 298.15, 308.15 and 318.15 K).

EXPERIMENTAL

Materials

L-serine (> 99 wt.%), S(+)-alanine (> 99 wt.%) and [C$_4$mim]Cl ($\geq$ 98 wt.%) were purchased from Merck. [C$_4$mim][CF$_3$SO$_3$] ($\geq$ 98 wt.%) was purchased from Aldrich. L-proline ($\geq$ 99.0 wt.%) was purchased from BDH. The chemical structures of the investigated amino acids and ILs along with water content of the ILs are represented in Table 1. Double distilled water was used.

Method of Measurement

All solutions were prepared by mass using an analytical balance (Sartorius, CP124S, Germany) with an uncertainty of $\pm 1 \times 10^{-7}$ kg. The water content in the studied ILs was measured using a microprocessor based automatic Karl-Fischer Titrator with precision of ± 3 ppm and was taken into account in the calculation of the global compositions of the investigated solutions. Density and sound velocity measurements were carried out using a high precision vibrating-tube analyzer and sound velocity measuring device (Anton Paar DSA 5000, Austria) with proportional temperature control keeping the solutions at working temperature within $\pm 10^{-3}$ K. Before each series of measurements, the instrument was calibrated with freshly degassed and double distilled water and dry air at atmospheric pressure according to the instrument catalog.

The instrument required a liquid volume of about 2.5 cm^3 and measured the density and sound velocity simultaneously after a thermal equilibration period of about 10 min. The experimental uncertainty in density and sound velocity measurements was obtained as $\pm 5 \times 10^{-5}$ g cm^{-3} and ± 0.5 m s^{-1}, respectively.

RESULTS AND DISCUSSION

In order to evaluate the influence of amino acids on the volumetric and compressibility properties of ILs in aqueous solutions, the density and sound velocity of [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] solutions in 5% w/w aqueous solutions of amino acids l-serine, s-alanine and l-proline were measured at T = 288.15, 298.15, 308.15 and 318.15 K. The measured density and sound velocity data are reported in Table S1 given as supporting information.
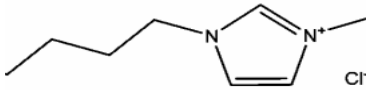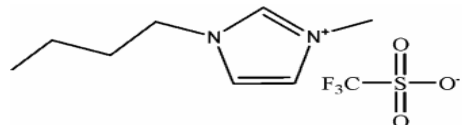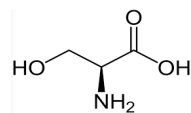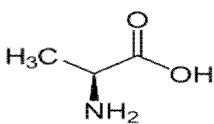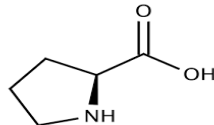
Apparent Molar Volume

The apparent molar volumes, V_ϕ^s, of the ILs in the solutions investigated at different temperatures were calculated from experimental density data using the following equation [28]:

$$V_\phi = \frac{1000\,(d_0 - d)}{mdd_0} + \frac{M}{d} \tag{1}$$

where, M and m are, respectively, the molar mass and the molality of the ILs, d and d_0 are the densities of solution and the solvent, respectively. For all the ternary (IL+ amino acid + H$_2$O) systems studied in this work, the amino acid + water (aqueous solutions of 0.05 w/w amino acid) was considered as the solvent. The concentration dependences of V_ϕ for [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in aqueous solutions of different amino acids at 298.15 K are shown in Figure 1. As can be seen from Fig. 1, the values of V_ϕ for [C$_4$mim]Cl in aqueous solutions of different amino acids slightly decrease with increase in the IL molality, while those of [C$_4$mim][CF$_3$SO$_3$] are approximately independent of the concentrations of IL. The values of the apparent specific volume, V_ϕ/M, increase in the order: [C$_4$mim][CF$_3$SO$_3$] < [C$_4$mim]Cl. This trend indicates that the apparent specific volume of Cl$^-$ is larger than CF$_3$SO$_3^-$. For ILs with more hydrophilic nature, the enhancement of the electrostriction

Table 1. Specification of the Chemicals Studied

Chemical	Purification method	Water content /ppm	Structure
[C$_4$mim]Cl	None	2330	
[C$_4$mim][CF$_3$SO$_3$]	None	3820	
Serine	None	-	
Alanine	None	-	
Proline	None	-	

effect of water in the hydration cosphere of IL will lead to reduce the apparent molar volume, thereby reducing the apparent specific volume of IL. However, [C$_4$mim][CF$_3$SO$_3$] with the higher molar mass has a lower apparent specific volume than [C$_4$mim]Cl. Figure 1 shows that the V_ϕ values of [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in the investigated aqueous amino acid solutions decrease in the order: serine > pure water (in the case of [C$_4$mim][CF$_3$SO$_3$]) > alanine > pure water (in the case of [C$_4$mim]Cl) > proline. These results indicate that the difference in the hydrophobic nature of the amino acids is responsible for the observed behaviour. Actually, as can be seen from Fig. 1, the effectiveness of the investigated amino acids in decreasing the V_ϕ of [C$_4$mim][CF$_3$SO$_3$] and [C$_4$mim]Cl in aqueous solutions increases with the hydrophobicities of amino acids. As an example, in Fig. 2, the temperature and concentration dependence of apparent

molar volume are presented for [C$_4$mim][CF$_3$SO$_3$] and [C$_4$mim]Cl in aqueous solutions 5% w/w of amino acids of alanine, and proline, respectively. It was found that the V_ϕ values increase by increasing temperature. The similar behaviors were observed for all other systems investigated in this study.

The values of the infinite dilution apparent molar volume of the ILs, which can be obtained by extrapolation of the experimental V_ϕ to zero molality, will be helpful in the fundamental understanding of the solute-solvent interactions. At infinite dilution, each molecule of the solute is surrounded only by the solvent molecules, and therefore, in this state only the solute-solvent interactions take place. The concentration dependence of V_ϕ values for both ILs were found to be linear, therefore, the infinite dilution apparent molar
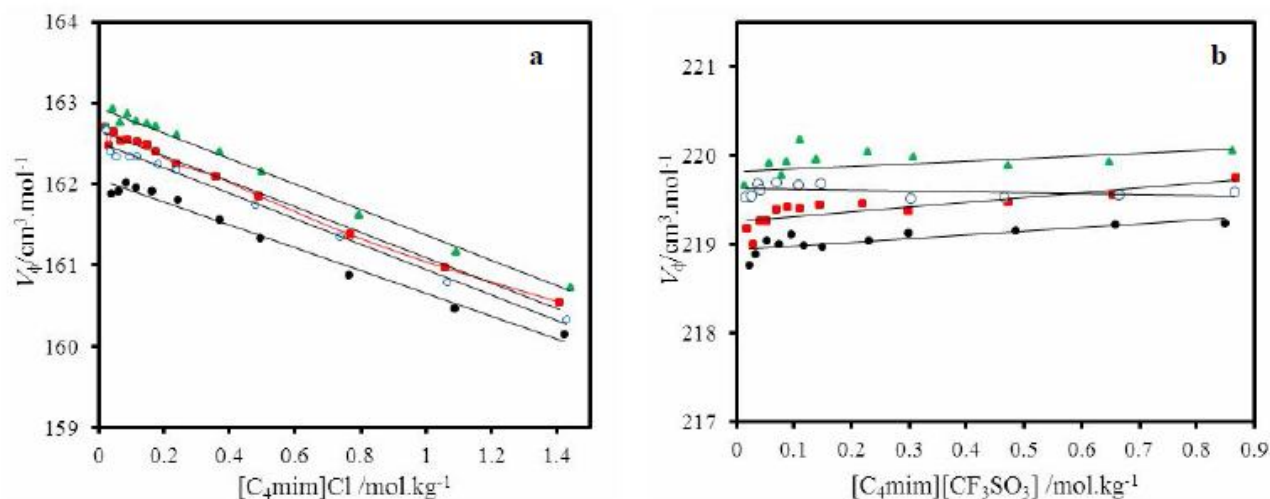
Fig. 1. Plot of apparent molar volume, $V_\square$, against molality of [C$_4$mim]Cl (a) and [C$_4$mim][CF$_3$SO$_3$] (b) in pure water and in aqueous solutions of 5% w/w of the amino acids at $T = 298.15$ K ; $\circ$, pure water [29]; $\bullet$, proline; $\blacksquare$, alanine; $\blacktriangle$, serine. Lines were calculated using Eq. (2).
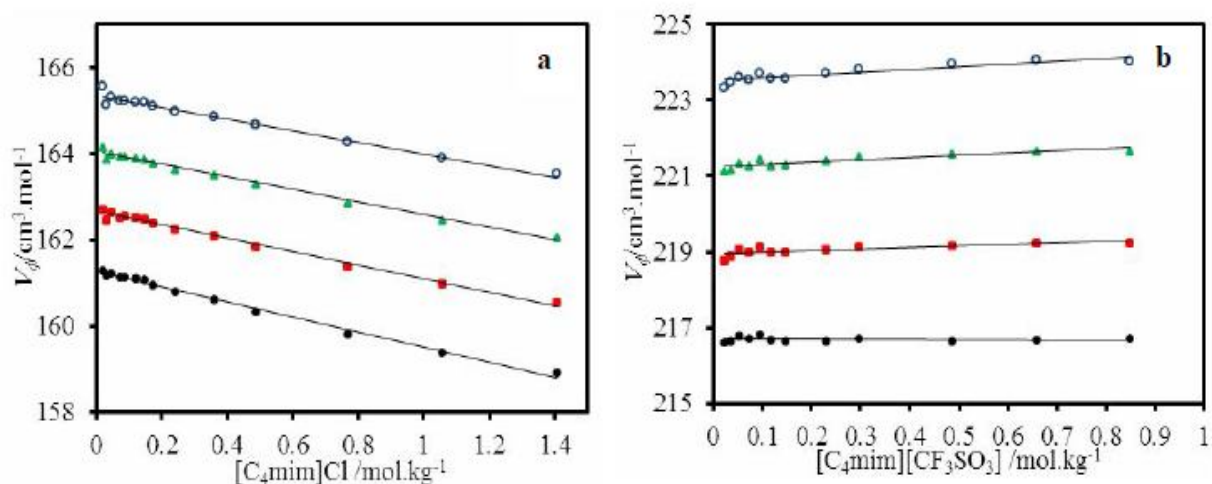

Fig. 2. Plot of apparent molar volume, $V_\square$, against molality of [C$_4$mim]Cl (a) and [C$_4$mim][CF$_3$SO$_3$] (b) in aqueous solutions of 5% w/w of the amino acids alanine and proline, respectively, at: $\bullet$, 288.15 K; $\blacksquare$, 298.15 K; $\blacktriangle$, 308.15 K; $\circ$, 318.15 K. Lines were calculated using Eq. (2).

volumes of the ILs, V_ϕ^0s, were obtained from the following linear relation between the apparent molar volumes and molalities [30]:

$$V_\phi = V_\phi^s + S_V m \qquad (2)$$

where S_V is an empirical parameter. The obtained values of V_ϕ^0 and S_V of the investigated systems at different temperatures are given in Table 2. The increase in V_ϕ^0 with temperature may be attributable to loosing the water molecules from the solvation layers of ILs in aqueous amino

Table 2. The Obtained Values of V_ϕ^0, S_V, K_ϕ^0 and S_K (Cefficients of Eqs. (2) and (8)) and Standard Deviation, σ, for Different Systems Investigated in This Work at Different Temperatures

|	V_ϕ^0	S_V	σ	$K_\phi^0 \times 10^5$	$S_k \times 10^5$	$\sigma \times 10^5$
	$cm^3\ mol^{-1}$	$cm^3\ kg\ mol^{-2}$	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}\ kPa^{-1}$	$cm^3\ kg\ mol^{-2}\ kPa^{-1}$	$cm^3\ mol^{-1}\ kPa^{-1}$
T (K)			[C$_4$mim]Cl in 5% w/w aqueous solution of alanine			
288.15	161.27 ± 0.02	-1.75 ± 0.04	0.06	-2.11 ± 0.03	0.9952 ± 0.05	0.07
298.15	162.66 ± 0.02	-1.56 ± 0.04	0.06	-0.70 ± 0.01	0.6881 ± 0.03	0.04
308.15	164.04 ± 0.02	-1.46 ± 0.04	0.06	0.32 ± 0.03	0.5528 ± 0.05	0.07
318.15	165.36 ± 0.03	-1.35 ± 0.06	0.08	1.19 ± 0.02	0.4261 ± 0.05	0.07
			[C$_4$mim]Cl in 5% w/w aqueous solution of proline			
288.15	160.64 ± 0.03	-1.5978 ± 0.05	0.07	-2.06 ± 0.05	0.8328 ± 0.08	0.10
298.15	162.06 ± 0.04	-1.4098 ± 0.06	0.08	-0.72 ± 0.04	0.5987 ± 0.07	0.09
308.15	163.49 ± 0.03	-1.3285 ± 0.05	0.07	0.31 ± 0.04	0.4437 ± 0.06	0.08
318.15	164.79 ± 0.03	-1.1911 ± 0.05	0.07	1.15 ± 0.03	0.3483 ± 0.05	0.07
			[C$_4$mim]Cl in 5% w/w aqueous solution of serine			
288.15	161.61 ± 0.02	-1.7682 ± 0.03	0.05	-1.98 ± 0.05	0.8332 ± 0.08	0.12
298.15	162.94 ± 0.03	-1.5682 ± 0.05	0.07	-0.60 ± 0.05	0.5660 ± 0.08	0.12
308.15	164.23 ± 0.02	-1.4325 ± 0.04	0.05	0.39 ± 0.02	0.4573 ± 0.04	0.05
318.15	165.47 ± 0.04	-1.2498 ± 0.06	0.09	1.24 ± 0.01	0.3545 ± 0.03	0.04
			[C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of alanine			
288.15	217.08 ± 0.03	0.0794 ± 0.10	0.08	-0.30 ± 0.02	3.2012 ± 0.05	0.04
298.15	219.25 ± 0.04	0.5481 ± 0.12	0.10	1.48 ± 0.01	2.6882 ± 0.04	0.03
308.15	221.49 ± 0.05	0.7830 ± 0.13	0.11	2.87 ± 0.01	2.3664 ± 0.03	0.03
318.15	223.70 ± 0.05	0.9937 ± 0.14	0.12	4.07 ± 0.01	2.1074 ± 0.03	0.03
			[C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of proline			
288.15	216.69 ± 0.03	-0.0153 ± 0.07	0.06	-0.45 ± 0.04	3.3235 ± 0.10	0.08
298.15	218.94 ± 0.03	0.4090 ± 0.09	0.08	1.41 ± 0.02	2.6797 ± 0.05	0.04
308.15	221.23 ± 0.04	0.5969 ± 0.10	0.08	2.83 ± 0.01	2.3022 ± 0.03	0.02
318.15	223.51 ± 0.04	0.7481 ± 0.12	0.10	4.01 ± 0.01	2.0818 ± 0.03	0.03
			[C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of serine			
288.15	217.72 ± 0.08	-0.0935 ± 0.19	0.16	-0.23 ± 0.03	3.1228 ± 0.09	0.07
298.15	219.82 ± 0.07	0.2924 ± 0.18	0.15	1.54 ± 0.02	2.5956 ± 0.05	0.04
308.15	221.92 ± 0.08	0.6178 ± 0.21	0.18	2.94 ± 0.02	2.2446 ± 0.05	0.04
318.15	223.82 ± 0.14	1.2140 ± 0.34	0.29	4.13 ± 0.02	1.9876 ± 0.04	0.04
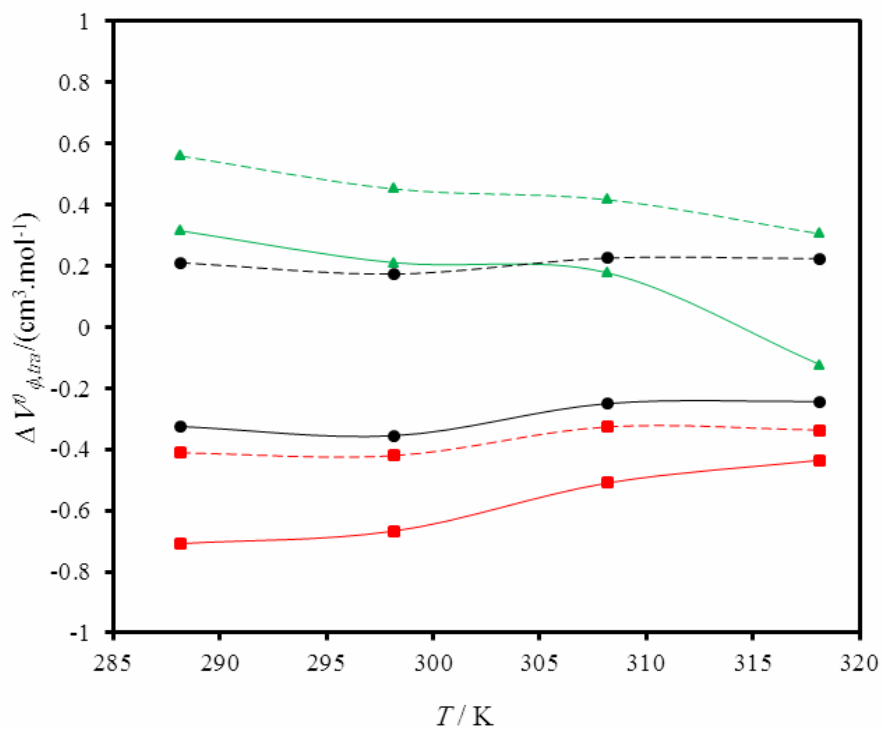
Fig. 3. Plot of the infinite dilution apparent molar volume of transfer of [C$_4$mim]Cl (solid lines), and [C$_4$mim][CF$_3$SO$_3$](dashed lines) from water to aqueous amino acid solutions, $\Delta V_{\phi,tra}^0$, against temperature; ■, proline; ●, alanine; ▲, serine.

acid solutions. Due to release some of the electrostricted water molecules to the bulk, the values of V_ϕ^0 increase by heating. As can be seen from Table 2 and Fig. 1, at the same conditions of temperature and the type of IL, the V_ϕ^0 values of [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in the investigated aqueous amino acid solutions follow the order: serine > pure water (in the case of [C$_4$mim][CF$_3$SO$_3$]) > alanine > pure water (in the case of [C$_4$mim]Cl) > proline. The effectiveness of the amino acids to reduce V_ϕ^0 of the studied ILs has a reverse order of the ability of these amino acids in salting-out of IL, which previously obtained as serine > alanine > proline according to the liquid–liquid equilibrium results [26]. The sharing of hydrophilic hydration co-sphere of zwitterions of amino acids (NH$_3^+$ and COO$^-$) and hydrophobic hydration co-sphere of the ILs will lead to increase V_ϕ^0 of the studied ILs. For amino acids with more hydrophilic nature, the effect of this factor is more than that

for the less hydrophilic amino acids. The similar behaviours were observed for the PPG725 in aqueous solutions containing these amino acids [31]. The S_V values of the ILs in different solutions can provide valuable information regarding the strength of the solute-solute interactions [32].

As can be seen from Table 2, for all the studied systems in this work, the S$_V$ values are smaller than V_ϕ^0 values, therefore it can be concluded that there is weak IL-IL interactions. From Table 2, it can also be seen that the S$_v$ values for [C$_4$mim]Cl in aqueous amino acid solutions, similar to its behavior in pure water [33-34], are negative and become less negative with increasing temperature. However, the S$_v$ values for [C$_4$mim][CF$_3$SO$_3$] in aqueous amino acid solutions (except at 288.15 K), similar to its behavior in pure water [33], are positive and become larger with increasing temperature.

The transfer apparent molar volumes at infinite

dilution, $\Delta V_{\phi,tr}^0$, for ILs from water to aqueous amino acid solutions have been calculated from the following equation:

$$\Delta V_{\phi,tr}^0 = V_\phi^0 \text{ (in aqueous a min o acid solution)} - V_\phi^0 \text{ (in water)}$$
(3)

V_ϕ^0 (in water) is the apparent molar volume at infinite dilution of IL in pure water, which was taken from the literature [29]. The temperature dependence of $\Delta V_{\phi,tr}^0$, for the investigated systems are shown in Figure 3. As can be seen, the $\Delta V_{\phi,tr}^0$ values for both [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in aqueous serine solutions are positive and in aqueous proline solutions are negative. However these values in aqueous alanine solutions are negative and positive, respectively, for [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$]. Furthermore the values of $\Delta V_{\phi,tr}^0$ for [C$_4$mim][CF$_3$SO$_3$] are larger than those for [C$_4$mim]Cl (increase with the hydrophobicity of the IL). The results reported in Figure 3 suggest that for the same IL in aqueous 5% w/w of the amino acid solution, V_ϕ^0 values decrease as the hydrophobicity of the amino acid increases and follow the order: serine > alanine > proline. The values of water activity in the binary amino acids + water solutions have been previously reported in the literature [26,35-37] and due to tendency of serine for self-association in the binary amino acid aqueous solutions follow the order: serine > alanine > proline. However, in the case of amino acid-IL aqueous solutions, this trend is not similar to that in the binary amino acids + water solutions and proline; because of a larger hydrocarbon portion in its structure, is more hydrophobic than the alanine and serine [29].

These results indicate that more water molecules released from the salvation layers of the proline than alanine and serine, and consequently, through enhancement of electrostriction effect of water in the hydration cosphere of IL will lead to negative $\Delta V_{\phi,tr}^0$. The cosphere overlap model [38] can also be used to explain this behavior in the amino acid-IL aqueous solutions. According to this model, the interactions occurring between ILs and amino acids can be classified as follows [22-23,39-40]: (i) ionic-hydrophilic interactions between hydrophilic group (NH$_3^+$, COO$^-$) of amino acid and the anions and cation of the IL; (ii)

hydrophobic-hydrophobic interactions between the hydrophobic portion of amino acid and the alkyl chain of the imidazolium cation of IL; (iii) ionic-hydrophobic interactions between the anions and cation of the IL and hydrophobic portion of amino acid; (iv) hydrophilic-hydrophobic interactions between hydrophilic groups of amino acid and the alkyl chain of the imidazolium cation of IL. According to this model, among the different interactions occurring between amino acid and IL, only the ionic-hydrophilic interaction can release some water molecules back to the bulk state, which can lead to positive values for $\Delta V_{\phi,tra}^0$, while the other interactions (ii - iv) due to the increased electrostriction effect of water in the hydration cosphere of IL lead to negative $\Delta V_{\phi,tra}^0$. As an example, the positive $\Delta V_{\phi,tra}^0$ values of [C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of alanine and serine show that the ionic-hydrophilic interaction is stronger than other interactions (ii - iv). However, the negative $\Delta V_{\phi,tra}^0$ values of [C$_4$mim]Cl in 5% w/w aqueous solution of alanine and proline indicate that the hydrophilic-hydrophobic, ionic - hydrophobic and hydrophobic-hydrophobic interactions are the predominant interactions. For both ILs in 5% w/w aqueous solution of alanine and proline, there exist the hydrophobic-hydrophilic interactions between the methyl and pyrrolidine groups of amino acid and the ions of IL. The similar trends for the $\Delta V_{\phi,tra}^0$ values in amino acid-IL aqueous solutions have been previously observed [22]. The attractive interactions between the amino acid and ILs induce the dehydration of IL, and therefore, increase V_ϕ^0. For [C$_4$mim][CF$_3$SO$_3$] with less hydrophilic nature, the effect of this factor is more than that for [C$_4$mim]Cl with more hydrophilic nature, and therefore, the values of $\Delta V_{\phi,tra}^0$ for [C$_4$mim][CF$_3$SO$_3$] are more than those for [C$_4$mim]Cl.

The V_ϕ^0 values were related to temperature according to the following equation:

$$V_\phi^o = a + bT^{0.5} + c\ln(T)$$
(4)

Then, the infinite dilution apparent molar expansibilities, E_ϕ^0, were calculated by differentiating Eq. (4) with respect to temperature as:

Table 3. Fitting Parameters, a, b and c of Eq.(4)

System	Parameters		
	a	b	c
[C$_4$mim]Cl in 5% w/w aqueous solution of alanine	-40.030	1.019	32.489
[C$_4$mim]Cl in 5% w/w aqueous solution of proline	-163.651	-2.669	65.260
[C$_4$mim]Cl in 5% w/w aqueous solution of serine	-177.072	-3.707	70.913
[C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of alanine	439.729	18.634	-95.164
[C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of proline	431.480	18.722	-94.040
[C$_4$mim][CF$_3$SO$_3$] in 5% w/w aqueous solution of serine	-362.720	-7.127	123.846
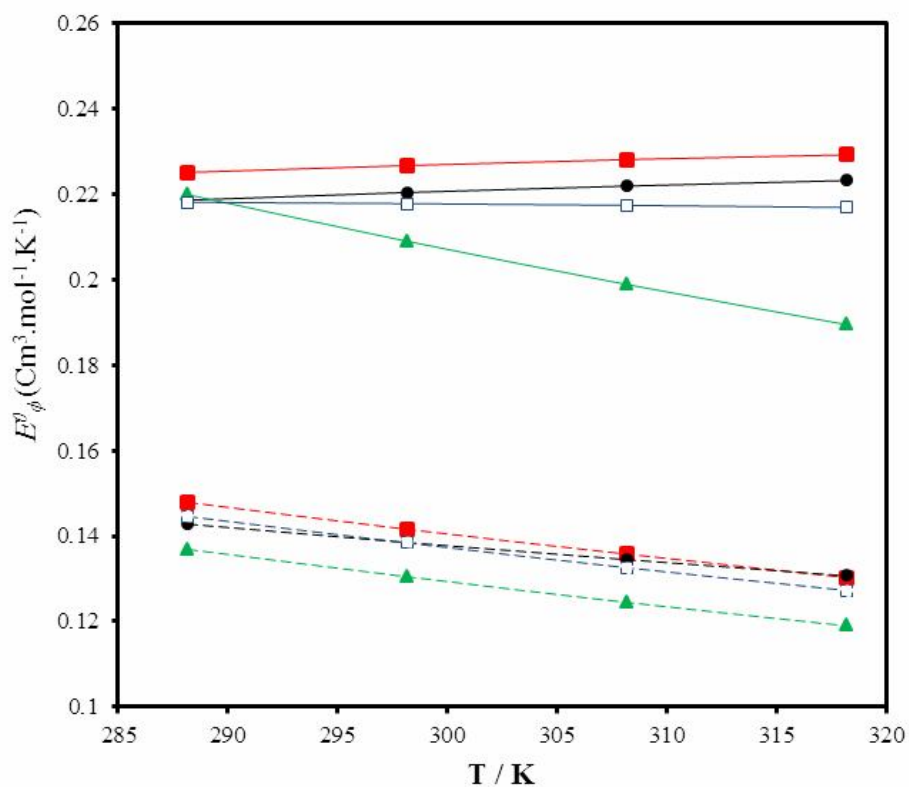
Fig. 4. Plot of the infinite dilution apparent molar expansibilities, E_ϕ^0 against temperature for [C$_4$mim]Cl (dashed lines), and [C$_4$mim][CF$_3$SO$_3$] (solid lines) in pure water and in aqueous 5% w/w of amino acid solutions at T = 298.15 K ; □, pure water [29]; ■, proline; ●, alanine; ▲, serine.

$$E_\phi^0 = \left(\frac{\partial V_\phi^0}{\partial T}\right)_P = \frac{b}{2T^{0.5}} + \frac{c}{T} \tag{5}$$

The obtained adjustable parameters a, b and c are given in Table 3.

As can be seen from Fig. 4, the positive values of E_ϕ^0 increase by increasing the hydrophobicity of ILs and at the same condition they follow the order: [C$_4$mim][CF$_3$SO$_3$] > [C$_4$mim]Cl. In fact, the positive expansibility values for the studied ternary mixtures, indicates that at higher temperatures some water molecules from the salvation layers of the ILs are released into the bulk of the water. Figure 4 also shows that for the investigated ILs in aqueous 5% w/w amino acid solutions, E_ϕ^0 values increase as the hydrophobicity of the amino acid increases and follows the order: proline > alanine > serine.

As $(\frac{\partial C_P^0}{\partial P})_T = -T(\frac{\partial^2 V_\phi^0}{\partial T^2})_P$, a positive value of $(\frac{\partial^2 V_\phi^0}{\partial T^2})_P$ seems to associate with a structure-making solute and a negative one is associated with a structure-breaking solute [41]. The results given in Fig. 5 show that the values of $(\frac{\partial E_\phi^0}{\partial T})_P = (\frac{\partial^2 V_\phi^0}{\partial T^2})_P$ for [C$_4$mim]Cl in aqueous amino acid solutions are negative, while those of [C$_4$mim][CF$_3$SO$_3$] (with the exception of [C$_4$mim][CF$_3$SO$_3$] in aqueous serine solutions) are positive. Furthermore, under the same conditions, the magnitude of $(\frac{\partial^2 V_\phi^0}{\partial T^2})_P$ and therefore the structure-breaking property of [C$_4$mim]Cl in the investigated solutions follow the order: serine ≈ proline > alanine.

Isentropic Compressibility

Values of the adiabatic compressibility, κ_s, of the investigated solutions were calculated based on the experimentally determined sound velocities and densities using the Laplace-Newton's equation:

$$k_S = \frac{1}{du^2} \tag{6}$$

where u is the speed of solution's sound. As shown in Fig. 6, the isentropic compressibility of all the investigated solutions decreases with increasing IL concentration. The decrease in κ_s values can be attributed to the effect of solute on the surrounding solvent molecules leading to increase in internal pressure which makes the solution harder to compress. This is due to the presence of strong solute-solvent interactions [42]. From Fig. 6, it can also be seen that the isentropic compressibility of the investigated aqueous IL solutions in the presence and absence of the investigated amino acids, at high IL concentrations, follows the order: [C$_4$mim][CF$_3$SO$_3$] > [C$_4$mim]Cl , which is the same order of their hydrophobicity. The values of κ_s for the IL-amino acid-H$_2$O systems are independent of type of the amino acid. Figure 6 also shows that the values of κ_s decrease by increasing temperature.

Apparent Molar Isentropic Compressibility

Apparent molar adiabatic compressibilities, κ_ϕs, of the solutes which defined as $K_\phi = -\left(\frac{\partial V_\phi}{\partial P}\right)_S$, were calculated for the ILs in aqueous solutions of the amino acids from the experimental density and sound velocity data by means of the following equations:

$$K_\phi = \frac{1000(k_S d_0 - k_S^0 d)}{mdd_0} + \frac{Mk_S}{d} \tag{7}$$

Figure 7 indicates the concentration dependence of κ_ϕ for [C$_4$mim]Cl in pure water and in aqueous 5% w/w amino acid solutions at $T = 298.15$ K. The negative values of κ_ϕ are related to the fact that the water molecules in the hydration layer of the solute are less compressible than those in the bulk. Because of the less hydrophobicity of [C$_4$mim]Cl than [C$_4$mim][CF$_3$SO$_3$], the values of κ_ϕ for [C$_4$mim]Cl are more negative than those for [C$_4$mim][CF$_3$SO$_3$]. Figure 7 also shows that the values of κ_ϕ increase by increasing temperature and IL concentration and those in the presence of the amino acids are larger than those in pure water. The infinite dilution apparent molar isentropic compressibilities, K_ϕ^0s, can be calculated from the κ_ϕ data using the following equation [43]:

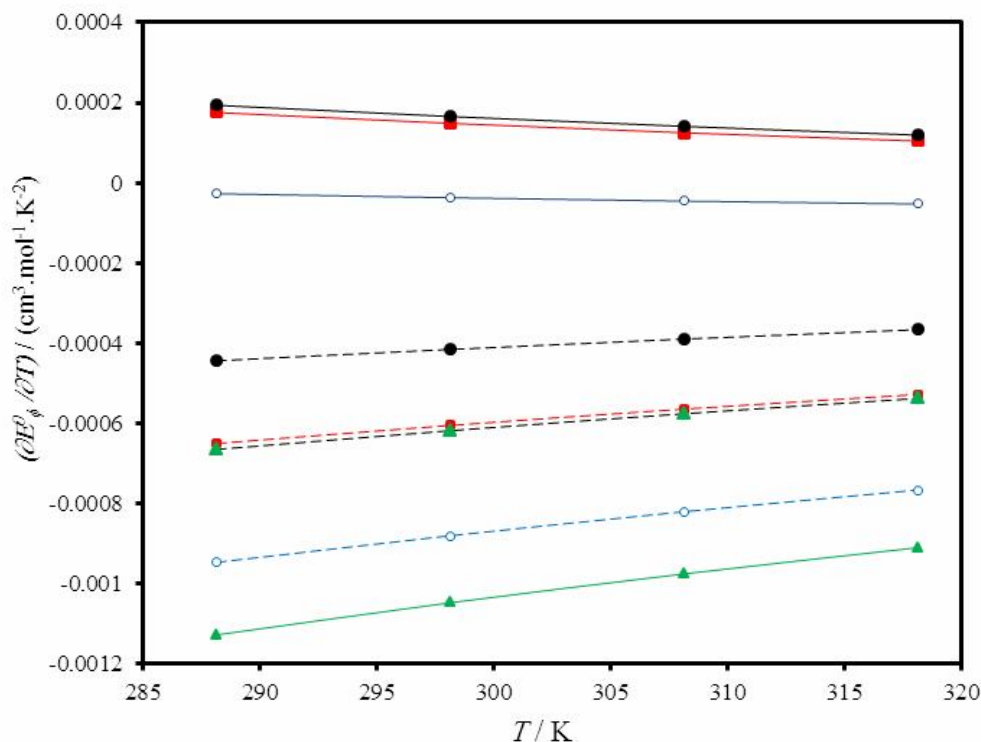$$K_\phi = K_\phi^0 + S_K m \tag{8}$$

Fig. 5. Plot of $(\frac{\partial E_\phi^0}{\partial T})_T$ against temperature for [C$_4$mim]Cl (dashed lines), and [C$_4$mim][CF$_3$SO$_3$] (solid lines) in pure water and in aqueous 5% w/w amino acid solutions at T = 298.15 K ; ○, pure water [29]; ■, proline; ●, alanine; ▲, serine.

The obtained values of K_ϕ^0 and S_k for the studied ILs in aqueous solutions of 5% w/w of the amino acids at different temperatures are also listed in Table 2. According to this table, the values of K_ϕ^0 at low temperatures are negative and become positive at higher temperatures. The K_ϕ^0 values become more positive with increase in temperature, which means that the electrostriction reduces and some water molecules are released to the bulk. At the same conditions, the K_ϕ^0 values of [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in the investigated aqueous amino acid solutions follow the order: serine > alanine > proline. The repulsive interactions between the amino acid and water molecules induce more hydration of the IL. For the amino acids with more hydrophobic nature, the effect of this factor is more than that for the amino acids with less hydrophobic nature, and therefore, the values of K_ϕ^0 for the ILs in 5% w/w aqueous

solution of proline is less than that in 5% w/w aqueous solutions of serine and alanine. As can be seen from Table 2, the experimental slopes S_k for [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in aqueous amino acid solutions are positive values. This behavior is indicative of the presence of weak solute-solute interactions in these solutions.

The changes in the apparent molar adiabatic compressibilities at infinite dilution, $\Delta K_{\phi,tr}^0$, for transfer of the ILs from water to aqueous amino acid solutions were calculated from the following equation:

$$\Delta K_{\phi,tr}^0 = K_\phi^0 \quad (\text{in aqueous amino acid solution}) \quad - K_\phi^0 \ (\text{in water})$$
(9)

Figure 8 shows that the obtained values of $\Delta K_{\phi,tr}^0$ for both ILs are positive and decrease as the temperature increases.
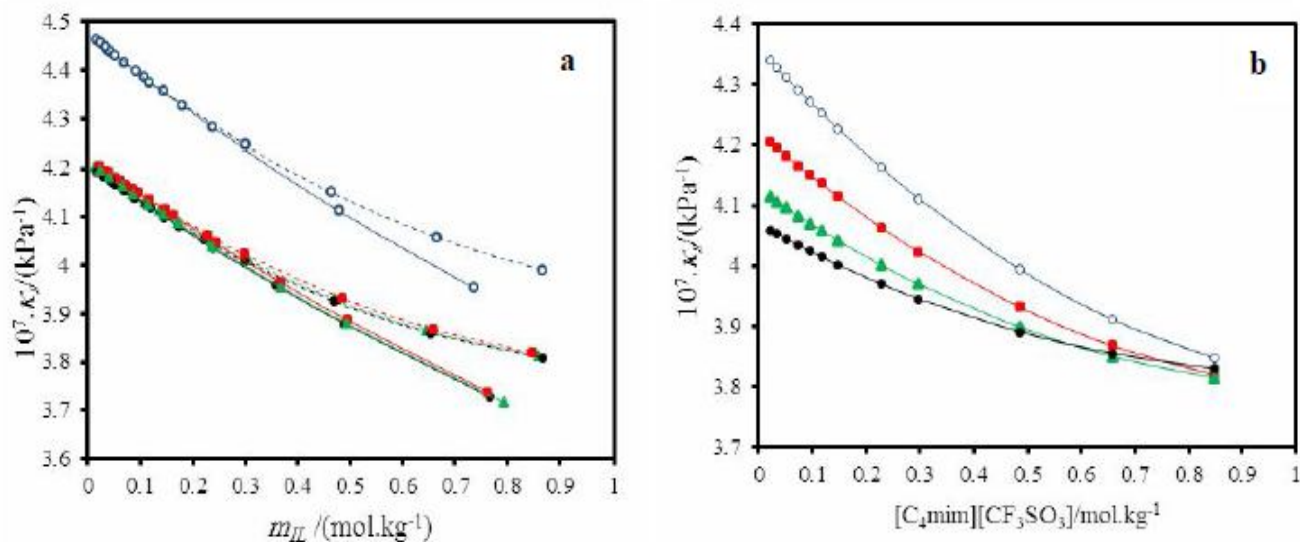
Fig. 6. a) Plot of isentropic compressibility, κ_s, for solutions of [C$_4$mim]Cl (solid lines) and [C$_4$mim][CF$_3$SO$_3$] (dashed lines) in pure water and in aqueous solutions of 5% w/w of the amino acids at T = 298.15 K: ○, pure water [29]; ■, proline; ●, alanine; ▲, serine. b) Plot of isentropic compressibility of solution, κ_s, against molality of [C$_4$mim][CF$_3$SO$_3$] in aqueous 5% w/w proline solutions at different temperatures: ○, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.
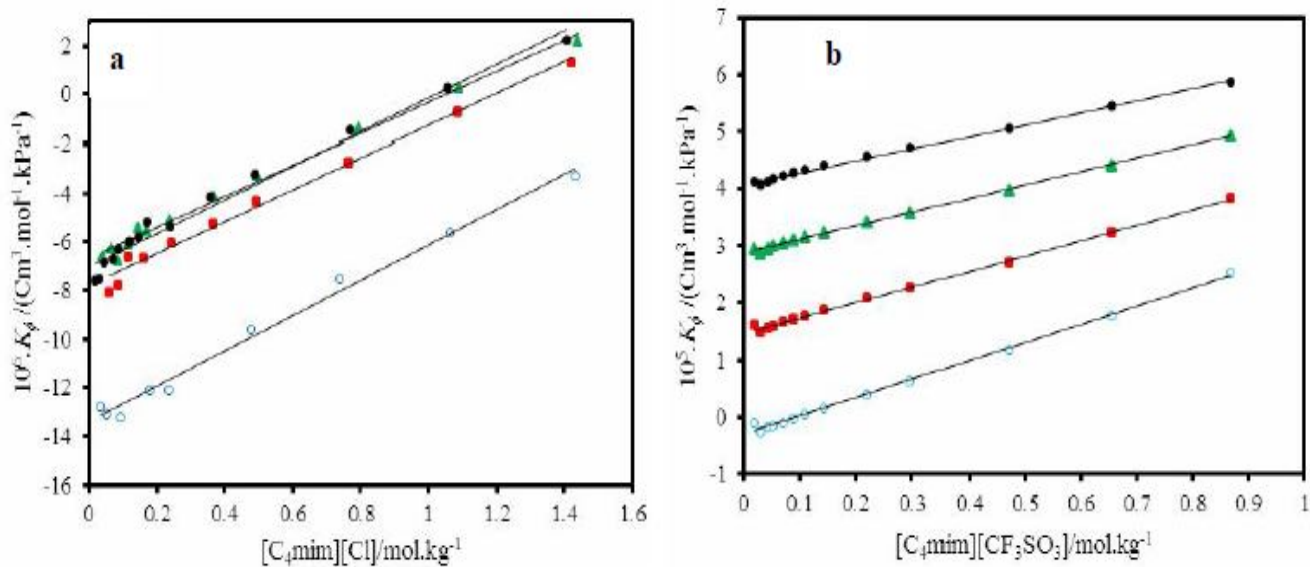

Fig. 7. a) Plot of apparent molar adiabatic compressibility, K_ϕ, against molality of [C$_4$mim]Cl in pure water and in aqueous 5% w/w amino acid solutions at T = 298.15 K ; ○, pure water [29]; ■, proline; ●, alanine; ▲, serine. b) The temperature dependence of apparent molar adiabatic compressibility of [C$_4$mim][CF$_3$SO$_3$] in aqueous 5% w/w alanine solutions as a function of molality of [C$_4$mim][CF$_3$SO$_3$]: ○, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K. Lines were calculated using Eq. (8).
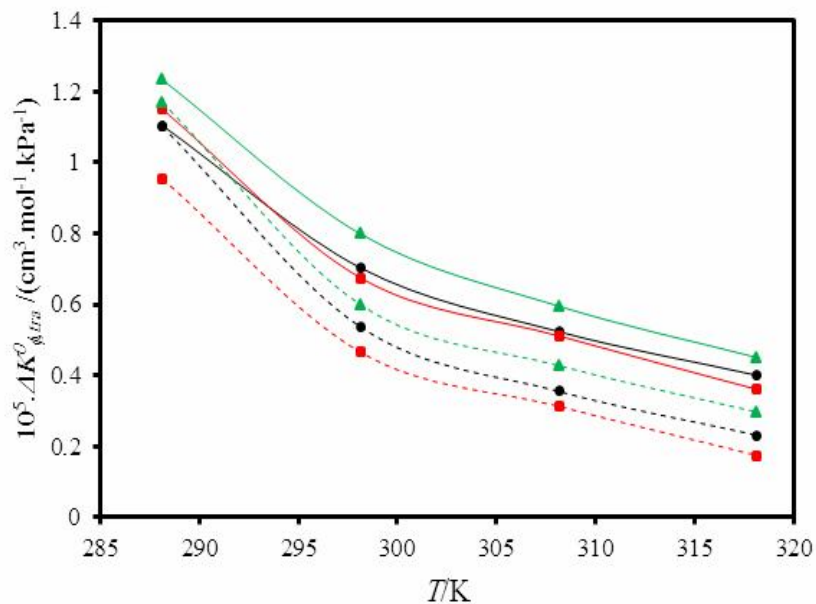
Fig. 8. Plot of infinite dilution apparent molar adiabatic compressibility for transfer of [C$_4$mim]Cl (solid lines) and [C$_4$mim][CF$_3$SO$_3$] (dashed lines) from water to aqueous 5% w/w amino acid solutions, $\Delta K_{\phi,tra}^0$, against temperature: ■, proline; ●, alanine; ▲, serine.
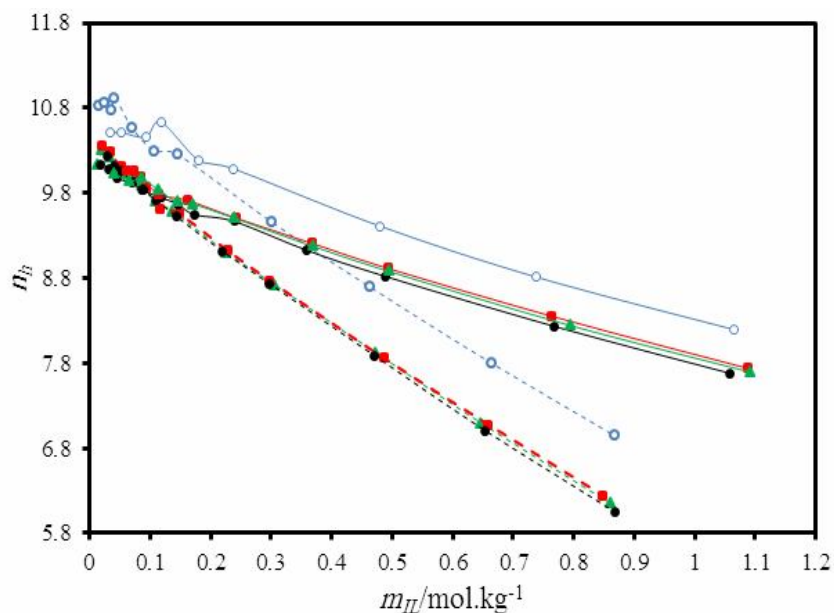

Fig. 9. Plot of hydration number, n_h, for solutions of [C$_4$mim]Cl (solid lines) and [C$_4$mim][CF$_3$SO$_3$] (dashed lines) in pure water and in aqueous 5% w/w of the amino acid solutions at T = 298.15 K, ○, pure water; ■, proline; ●, alanine; ▲, serine.
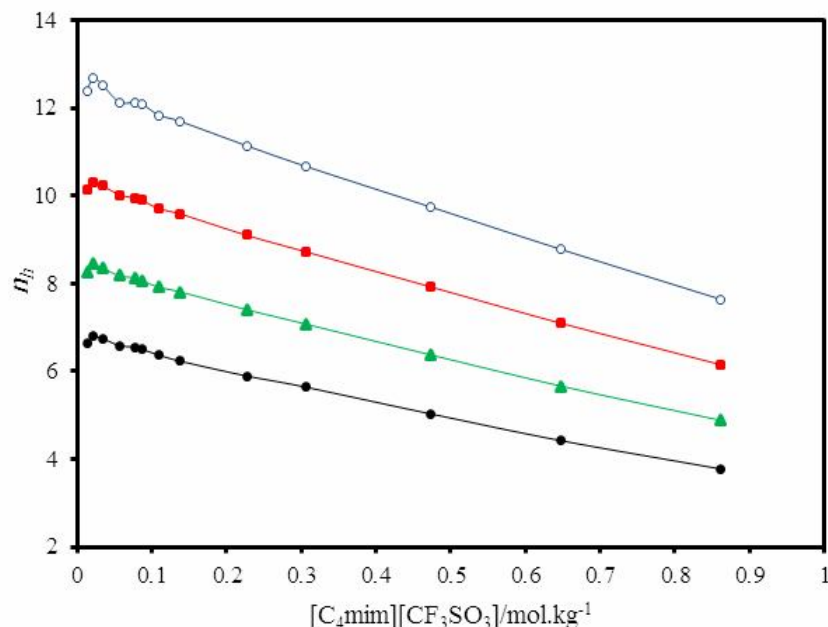
Fig. 10. Plot of hydration number, n_h, for [C$_4$mim][CF$_3$SO$_3$] in aqueous 5% w/w of serine solutions at different temperatures: ○, 288.15 K; ■, 298.15 K; ▲, 308.15 K; ●, 318.15 K.

The positive values of $\Delta K^0_{\phi,tr}$ of the ILs may be attributed to the release of a more amount of water molecules from the secondary solvation layer of the IL into the bulk water. It was found that the values of $\Delta K^0_{\phi,tr}$ for [C$_4$mim]Cl are larger than those for [C$_4$mim][CF$_3$SO$_3$]. Figure 8 also shows that the values of $\Delta K^0_{\phi,tr}$ for transfer of ILs from pure water to aqueous amino acids solutions decrease in the order: serine > alanine > proline.

Hydration Number

The hydration numbers (n_h) of the investigated ILs were calculated using the method reported by Passynski [44] for aqueous electrolyte solutions:

$$n_h = \frac{n_1}{\left(n_2\left(1 - \frac{k_s}{k_s^0}\right)\right)} \tag{10}$$

where n_1 and n_2 are the number of moles of solvent and solute (IL), respectively. κ_s and κ_s^0 are the isentropic compressibility of solution and solvent, respectively. Figure

9 indicates that the hydration number decreases with increasing IL concentration, which is indicative of the ion-association at higher concentrations. The calculated values of the hydration number decreased in the presence of the studied amino acids, which can be attributed to the favorable IL-amino acid interactions, followed by the release of some water molecules from the hydration layer of the solutes into the bulk state. Figure 9 also shows that the hydration numbers of the investigated systems follow the order: [C$_4$mim]Cl > [C$_4$mim][CF$_3$SO$_3$] which is in consistent with the degree of hydrophilicity of the ILs. As can be seen from Fig. 10, the values of the hydration number decrease by increasing temperature. This can be attributed to a loss of hydration by heating.

CONCLUSIONS

The volumetric and acoustic properties of aqueous solutions of the ILs [C$_4$mim]Cl and [C$_4$mim][CF$_3$SO$_3$] in the aqueous solutions of 5% w/w of the amino acids of serine, alanine and proline have been obtained from the experimental density and speed of sound data at T = (288.15

to 318.15) K. The different amino acids have affected in decreasing V_ϕ of ILs in the order: serine < alanine < proline, corresponding to the increase in hydrophobicity of the amino acids. For both of the studied ILs, the infinite dilution partial molar volume, V_ϕ^0, and infinite dilution partial molar isentropic compressibility, K_ϕ^0, increase as temperature increases. The hydration number of the investigated aqueous IL solutions in the absence and presence of investigated amino acids follows the order: $[C_4mim]Cl > [C_4mim][CF_3SO_3]$, in consistent with the degree of hydrophilicity of the ILs. The negative values of $(\frac{\partial E_\phi^0}{\partial T})_p$ for $[C_4mim]Cl$ in aqueous amino acid solutions indicates the structure- breaking property of this solute. The values of $\Delta K_{\phi,tr}^0$ for transfer of $[C_4mim]Cl$ and $[C_4mim][CF_3SO_3]$ from water to aqueous amino acid solutions are positive and decrease as the temperature increases.

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