

Effect of 1-Butyl-3-methylimidazolium Ibuprofenate as an Active Pharmaceutical Ingredient Ionic Liquid (API-IL) on the Thermodynamic Properties of Glycine and L-Alanine in Aqueous Solutions at Different Temperatures

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Abstract Recently, ionic liquids have been combined with active pharmaceutical ingredients (APIs), and a third generation of ILs has emerged (API-ILs). The effect of a novel ionic liquid containing the ibuprofenate anion as an active pharmaceutical ingredient ionic liquid (API-IL) on the thermodynamic properties of two amino acids, glycine and L-alanine, have been studied. The densities, speeds of sound, viscosities and refractive indices of glycine and L-alanine in water and in aqueous solutions of an API-IL, 1-butyl-3-methylimidazolium ibuprofenate ([BMIM][Ibu]), have been determined at temperatures 288.15–318.15 K. The measured data have been used to calculate the standard partial molar volume V_{ϕ}^0 , partial molar volume of transfer $\Delta_{tr} V_{\phi}^0$, Hepler's constant $(\partial^2 V_{\phi}^0/\partial T^2)_p$, apparent molar isentropic compressibility κ_{ϕ} , molar refraction R_D , viscosity *B* coefficient (*B*) and hydration number parameters $n_{\rm H}$. All of these parameters are discussed in terms of the competitive interactions occurring between amino acids–[BMIM][Ibu] and amino acids–water.

Keywords 1-Butyl-3-methylimidazolium ibuprofenate \cdot Apparent molar volume \cdot Viscosity *B* coefficient \cdot Hydration number \cdot Refractive index

1 Introduction

Ibuprofen is a common nonsteroidal anti-inflammatory pharmaceutical (NSAID) applied for treating fever, reducing inflammation and relieving pain. The solubility of its natural form in water is less than $1 \text{ mg} \cdot \text{mL}^{-1}$ which results in its low bioavailability [1]. Many

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approaches have been proposed to improve the oral bioavailability. One of these ways is the formation of a salt form of active pharmaceutical ingredients (APIs). The sodium salt of ibuprofen is mainly employed to enhance its water solubility. Unfortunately, this approach has several problems including lack of salt formation and rapid hydrolysis from humidity in air. This salt may convert back to their original acid, which leads to aggregation in the gastrointestinal tract [2–4]. To overcome the potential problems with solidstate active pharmaceutical ingredients (APIs), such as solubility and bioavailability, pure liquid salt (ionic liquid) forms of active pharmaceutical ingredients (API-ILs) are now considered as a design strategy [5]. Also, the use of an active pharmaceutical ingredient in the liquid form at room temperature can avoid some of the issues of polymorphism associated with crystalline solids that dramatically affect the drug's solubility and dosages [6–8].

Recently, ILs have been combined with active pharmaceutical ingredients (API-ILs) and a third generation of ILs has appeared [7]. These API-ILs compounds present improved properties, such as increased stability, solubility, permeability and drug delivery, as compared to the corresponding solid pharmaceutical forms [7–9]. Viau and co-worker synthesized new ionogels by a one step sol–gel method using 1-butyl-3-methyl-imida-zolium ibuprofenate ([BMIM][Ibu]) and silica precursor [10]. These new ionogels open a large field of applications in drug delivery due to their simple preparation and the wide range of possible ILs [10].

A number of dual biological-functioning API-ILs, such as benzalkonium ibuprofenate, benzalkanium sulfacetamide and lidocaine ducustate, were first synthesized by Rogers and co-workers [9]. Results showed that benzalkanium ibuprofenate [BA][ibuprofenate] is active against various types of bacteria and the LD, in comparison with LHCl, was more effectively absorbed through the skin of a mouse's tail [11, 12].

API-IL macromolecular interactions involved in API transport and protein are an important topic in physiological media. Binding API with proteins affects the structure of the proteins as well as their properties such as activity of the enzymes, stability and solubility of these complex molecular compounds [13–15]. Direct study of the proteins is difficult due to their complex molecular structure. Therefore, the study of simpler model compounds such as amino acids, which are building blocks of proteins, is a useful approach [16, 17].

To optimize and control biotechnological processes including protein hydration, determining the conformational stability, activity of enzymes, denaturation and solubility of these compounds, studies on the thermodynamic and transport properties of API-IL in aqueous biomolecule (proteins, enzymes and hormones) solutions are needed. As far as we know, despite the importance of active pharmaceutical ingredients, there is no thermodynamic data for API-ILs in the presence of amino acids.

In recent years, mixtures containing an amino acid and ionic liquid have been studied in aqueous media at different temperatures. Shekaari and co-worker [18–20] have reported densities, viscosities, electrical conductance and refractive indices of amino acids (glycine, L-alanine and L-valine) in aqueous solutions of some imidazolium-based ionic liquid. They observed positive $\Delta_{tr} V_{\phi}^0$ values for glycine and negative $\Delta_{tr} V_{\phi}^0$ values for L-alanine and L-valine in (1-hexyl and 1-propyl)-3-methylimidazolium bromide. Fang and co-worker [21] have also reported negative $\Delta_{tr} V_{\phi}^0$ values for glycine, L-alanine, and L-phenylalanine in the presence of 1-ethyl-3-methylimidazolium bromide. Roy and co-worker [22] have also reported the solvation behavior of amino acids in aqueous solutions of tetrabutylphosphonium tetrafluoroborate at 298.15 K.

Therefore, in the present work, density, speed of sound, viscosity and refractive index data for glycine and L-alanine have been measured in the presence of aqueous solutions of 1-butyl-3-methylimidazolium ibuprofenate, [BMIM][Ibu], at the experimental temperatures T = 288.15, 298.15, 308.15 and 318.15 K and at atmospheric pressure. The apparent molar volume, standard partial molar volume V_{ϕ} , partial molar volume of transfer $(\Delta_{tr}V_{\phi}^{0})$ and Hepler's constant $(\partial^{2}V_{\phi}^{0}/\partial T^{2})_{p}$ have been calculated using density data. Also, the apparent molar isentropic compressibilities κ_{s} have been computed from the experimental speed of sound data. The viscosity *B* coefficients were calculated using the viscosity of the solutions and their solvents. The measured experimental refractive index n_{D} data of the studied solutions were used for calculation of the molar refraction R_{D} . The results are interpreted on the basis of different types of competing solute–solvent interactions.

2 Experimental

2.1 Chemicals

The origin, CAS number, purification method, purity, method of purity determination and water content of the used chemicals are given in Table 1. The water content of the amino acids was determined using a biaperometric Karl–Fischer titrator (Metrohm 756 KF), and the values are approximately 0.03 % for glycine and 0.04 % for L-alanine. The physical properties of the synthesized ionic liquid, 1-butyl-3-methylimidazolium ibuprofenate, are also listed in Table 2. Doubly distilled deionized water was used with a specific conductivity less than 1 μ S·cm⁻¹ at 298.15 K.

2.2 Synthesis of the Ionic Liquid

The ionic liquid, 1-butyl-3-methylimidazolium ibuprofenate [BMIM][Ibu] was prepared from 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and sodium ibuprofen. 1-Butyl-3-methylimidazolium chloride was synthesized and purified according to standard procedures described in the [23–25]. Briefly, [BMIM][Cl] was synthesized by direct alkylation of *N*-methylimidazole, 0.05 mol (freshly distilled) with an excess of 1-chlorobutane (0.06 mol) to which *N*-methylimidazole was added drop wise over 1 h with vigorously

Chemical name	CAS No.	Provenance	Purity (mass fraction)	Structure	Purification method
Glycine	56-40-6	Merck	>0.99	H ₂ NOH	Non
L-Alanine	56-41-7	Merck	>0.99	H ₃ C OH	Non
N-methylimidazole	616-47-7	Merck	>0.99	-	Non
1-Chlorobutane	109-69-3	Merck	≥0.99		Non
Ibuprofen sodium	4-93-31121	Sigma Aldrich	≥ 0.98		Non
Ethyl acetate	141-78-6	Merck	>0.998		Non
Acetone	1-64-7	Merck	≥0.998		Non

Table 1 Description of the chemicals used

[BMIM][Ibu]	<i>T</i> /K	$d/10^{-3} (\text{kg} \cdot \text{m}^{-3})$	$u/m \cdot s^{-1}$	n _D
	288.15	1.035218	1647.05	1.5212
	298.15	1.028993	1602.19	1.5174
	308.15	1.022791	1555.25	1.5138
	318.15	1.016615	1510.54	1.5101

Table 2 Density (*d*), speed of sound (*u*) and refractive index (n_D) data for [BMIM][Ibu] at experimental temperatures and 0.0868 MPa^a

^a Standard uncertainties for $u(n_D) = 5 \times 10^{-4}$, u(T) = 0.01 K, u(p) = 0.01 MPa and relative uncertainty u_r for density is $u_r(d) = 0.005$ and for speed of sound is $u_r(u) = 0$

stirring, all in a two-necked round bottom flask placed in a ice bath. Then the mixture, already turbid, was refluxed for 72 h under a nitrogen atmosphere at 343 K. The crude product was decanted from hot solution in a separating funnel and washed four times with 50 mL of ethyl acetate. The product was dried at 353 K for at least 4 h at reduced pressure (0.7 kPa) using a rotary evaporator, followed by high vacuum desiccation (0.1 Pa) for at least 12 h to remove trace amounts of moisture. Water contents found in the ionic liquids by the Karl Fischer method were less than mass fraction 0.05 %.

The ionic liquids were analyzed by ¹H NMR and IR spectroscopies to confirm the absence of any major impurities and they were in fairly good agreement with those reported in the literature [24]. For the synthesis of 1-butyl-3-methylimidazolium ibuprofenate, 0.3 mol sodium ibuprofen was dissolved in ethanol and added slowly to 0.3 mol [BMIM][Cl] dissolved in a minimum amount of ethanol. The resulting mixture was stirred at 343 K for 3 h and then overnight at room temperature. The solution was filtered using a sintered glass funnel (pro 4 Germany), then 100 mL of dry acetone was added leading to the precipitation of NaCl, which was removed by filtering, and the solvent was removed under vacuum. Addition of acetone was continued until no further precipitation of NaCl could be detected. The product was then dried under vacuum at 333 K for 12 h. The product was obtained as a yellowish viscous liquid [25]. The sample was characterized by ¹H, ¹³C NMR and IR. The water content of the IL was determined using a coulometric Karl Fischer titrator (Metrohm 756 KF), and the value was approximately 0.05 % in mass fraction. The sample was characterized by ¹H and ¹C NMR and IR (see SI).

2.3 Apparatus and Procedure

The solutions were prepared by weight, using an analytical balance (AND, GR202, Japan) with an uncertainty $\pm 3 \times 10^{-8}$ kg on the molality basis, in glass vials closed tightly with parafilm. The uncertainty for molalities of the solutions is $\langle 3 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$. The water content in the ionic liquid and amino acids was taken into account during the preparation of aqueous solutions. The sample density *d* and speed of sound *u* were measured with a vibrating-tube densimeter (Anton Paar, DSA 5000 densimeter and speed of sound analyzer) at the approximate frequency of 3 MHz. The apparatus was calibrated with doubly distilled deionized and degassed water and dry air at atmospheric pressure. Density and speed of sound are very sensitive to temperature, so the temperature was kept constant within $\pm 10^{-3}$ K using the Peltier thermostat built into the densimeter. In each

measurement, the relative uncertainty of density and speed of sound are $\pm 1 \times 10^{-3}$ and 0.07, respectively [26].

An Anton Paar Rolling-ball Viscometer, Lovis 2000 M/ME, was used to determine viscosities of the solutions. The temperature was controlled to ± 0.005 K by a built in Peltier thermostat. The measurement of viscosities with the Lovis 2000 M/ME is based on the falling ball principle. A calibrated glass capillary with a steel ball as supplied by manufacturer; the Lovis 2000 M/ME was filled with the sample for measuring the ball falling time. The ball falling time and densities were used to estimate kinematic as well as dynamic viscosities. The calibration of capillary was performed by the manufacturer using viscosity standard fluids. In each measurement, the uncertainty of the viscosity is 0.006 mPa·s.

Refractive indices n_D of the studied solutions were determined using a digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of $\pm 5 \times 10^{-4}$. The instrument was calibrated with doubly distilled water before each series of measurements. A procedure called "zero setting" was always performed before the actual measurements of the sample's refractive index, to ensure that the refractometer was working properly. Calibration was made with pure liquids of known refractive index such as hexane. The temperature was controlled using a circulating bath thermostat (Cooling Bath 490, Iran) with a thermal stability of ± 0.01 K.

3 Results and Discussion

3.1 Volumetric Properties

The values of density *d* for glycine in water and in aqueous solutions of 0.1090, 0.1801 and 0.2642 mol·kg⁻¹ [BMIM][Ibu], along with density values for L-alanine in water and in aqueous solutions of 0.1110, 0.1800 and 0.2602 mol·kg⁻¹ [BMIM][Ibu], are reported in Table 3. The densities of the amino acids in water and in aqueous [BMIM][Ibu] solutions increase with the solute (amino acid) as well as with the co-solute ([BMIM][Ibu]) concentrations but decrease with increasing temperature. The density values of glycine and L-alanine in water at the experimental temperatures are in fairly good agreement with values reported in the literature (see Fig. S1 and S2 in the supporting information [26–29]). The values of density were used to calculate apparent molar volumes V_{ϕ} using:

$$V_{\varphi} = \frac{M}{d} - \left[\frac{(d-d_0)}{mdd_0}\right] \tag{1}$$

where *m* is the molality of the amino acids in water and in the aqueous solutions of [BMIM][Ibu], *M* is the molar mass of the amino acid, and d_0 and *d* are the densities of the solvent and solution.

The values of V_{ϕ} for the studied solutions are reported in Table 3. The experimental values of apparent molar volume of amino acids (glycine and L-alanine) in water at experimental temperatures are in good agreement with literature values [30–43]. A plot of V_{ϕ} for L-alanine in aqueous solutions of 0.1800 mol·kg⁻¹ [BMIM][Ibu] at T = 288.15, 298.15, 308.15 and 318.15 K is shown in Fig. 1. The values of V_{ϕ} for glycine in water and in aqueous solutions of 0.1801 and 0.2642 mol·kg⁻¹ [BMIM][Ibu] at T = 298.15 K are presented in Fig. 2. It is observed that the apparent molar volumes increase with increasing concentration of the ionic liquid. The standard partial molar

$ \begin{array}{l l l l l l l l l l l l l l l l l l l $	$m/(\text{mol}\cdot\text{kg}^{-1})^{\text{b}}$		$10^{-3} d/(1)$	kg·m ⁻³)			$10^{6} V_{\phi} / (1)$	$m^3 \cdot mol^{-1})$	
		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
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Glycine + water								
	0.0000	0.999094	0.997045	0.994025	0.990190				
	0.1142	1.002802	1.000645	0.997602	0.993715	42.44	43.41	43.65	44.16
	0.1525	1.004038	1.001841	0.998772	0.994873	42.44	43.44	43.80	44.28
	0.1962	1.005439	1.003197	1.000103	0.996214	42.47	43.48	43.90	44.23
	0.2484	1.007074	1.004793	1.001674	0.997763	42.61	43.57	44.01	44.38
	0.3032	1.008782	1.006452	1.003334	0.999393	42.71	43.67	44.03	44.44
	0.3537	1.010319	1.007976	1.004869	1.000884	42.86	43.72	44.01	44.49
	0.4004	1.011771	1.009373	1.006228	1.002284	42.87	43.78	44.13	44.46
	0.4496	1.013266	1.010806	1.007663	1.003705	42.95	43.89	44.21	44.54
$ 0.000 1.001449 0.999102 0.99517 0.91804 \\ 0.1140 1.005102 1.002672 0.993599 0.995309 42.85 43.61 43.81 44.28 \\ 0.1537 1.006360 1.003897 1.000575 0.996511 42.90 43.68 43.90 44.35 \\ 0.2080 1.008057 1.005852 1.002222 0.998140 43.00 43.56 44.10 44.43 \\ 0.2520 1.008457 1.005852 1.002322 0.99444 43.05 43.79 44.10 44.45 \\ 0.2070 1.010811 1.008252 1.00781 1.00781 43.12 43.86 44.16 44.55 \\ 0.2944 1.013963 1.01282 1.007821 1.00781 43.12 43.86 44.16 44.55 \\ 0.3997 1.013963 1.01282 1.007812 1.007744 43.20 44.07 44.35 44.46 \\ 0.3997 1.013963 1.011282 1.007812 1.007141 43.23 43.19 44.16 44.56 \\ 0.3997 1.013963 1.011282 1.007812 1.007141 43.23 44.17 44.35 44.66 \\ 0.3997 1.013963 1.011282 1.009240 1.005111 43.23 44.12 44.45 44.66 \\ 0.0000 1.0013280 1.0102442 0.992953 43.12 44.12 44.16 44.56 44.50 \\ 0.0000 1.003280 1.0102642 0.997141 0.992953 43.25 43.76 44.12 44.46 44.60 44.53 44.50$	Glycine + 0.1090) ^b mol·kg ⁻¹ [BMIN	M][Ibu] + water						
$ 0.1140 1.005102 1.002672 0.99359 0.995309 42.85 43.61 43.81 44.38 \\ 0.1537 1.006360 1.003897 1.00575 0.996511 42.90 43.68 43.90 44.35 \\ 0.2080 1.008057 1.005852 1.002222 0.998140 43.00 43.79 44.00 44.43 \\ 0.2520 1.008457 1.005855 1.002322 0.998140 43.05 43.85 44.12 44.55 \\ 0.2970 1.010811 1.008252 1.007812 1.00781 43.12 43.86 44.16 44.55 \\ 0.23499 1.012452 1.009821 1.006442 1.00781 43.12 43.86 44.16 44.55 \\ 0.3997 1.013963 1.01282 1.007892 1.007744 43.20 44.07 44.35 44.56 \\ 0.3997 1.013963 1.012662 1.009240 1.005111 43.23 44.12 44.36 \\ 0.467 1.015390 1.012662 1.009240 1.005111 43.23 44.12 44.35 44.36 \\ 0.467 1.015390 1.012662 1.009240 1.005111 43.23 44.12 44.35 44.46 \\ 0.0000 1.003280 1.012662 1.009240 1.005111 43.23 44.12 44.35 44.46 \\ 0.0000 1.003280 1.000646 0.997141 0.992963 43.25 43.76 44.16 44.46 \\ 0.0000 1.003283 1.000246 0.997141 0.992963 43.25 43.76 44.12 44.46 4$	0.0000	1.001449	0.999102	0.995817	0.991804				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	0.1140	1.005102	1.002672	0.999359	0.995309	42.85	43.61	43.81	44.28
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.1537	1.006360	1.003897	1.000575	0.996511	42.90	43.68	43.90	44.35
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.2080	1.008057	1.005552	1.002222	0.998140	43.00	43.79	44.00	44.44
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.2520	1.009425	1.006885	1.003532	0.999444	43.05	43.85	44.12	44.52
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.2970	1.010811	1.008252	1.004882	1.000781	43.12	43.86	44.16	44.55
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.3499	1.012452	1.009821	1.006442	1.002322	43.13	43.98	44.26	44.66
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.3997	1.013963	1.011282	1.007892	1.003744	43.20	44.07	44.35	44.78
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	0.4467	1.015390	1.012662	1.009240	1.005111	43.23	44.12	44.46	44.80
0.0000 1.003280 1.000646 0.997141 0.992963 0.1075 1.006681 1.003983 1.000449 0.996254 43.25 43.76 44.12 44.40 0.1501 1.008016 1.005290 1.001748 0.997532 43.28 43.85 44.10 44.53	Glycine + 0.1801	1 mol·kg ⁻¹ [BMIM	[][Ibu] + water						
0.1075 1.006681 1.003983 1.000449 0.996254 43.25 43.76 44.12 44.40 0.1501 1.008016 1.005290 1.001748 0.995322 43.28 43.85 44.10 44.53	0.0000	1.003280	1.000646	0.997141	0.992963				
0.1501 1.008016 1.005290 1.001748 0.997532 43.28 43.85 44.10 44.53	0.1075	1.006681	1.003983	1.000449	0.996254	43.25	43.76	44.12	44.40
	0.1501	1.008016	1.005290	1.001748	0.997532	43.28	43.85	44.10	44.53

Table 3 continue	p							
$m/(\text{mol}\cdot\text{kg}^{-1})^{b}$		$10^{-3} dl(1)$	kg·m ⁻³)			$10^{6} V_{\varphi} / (r$	$n^3 \cdot mol^{-1}$)	
	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
0.2013	1.009601	1.006856	1.003292	90666.0	43.35	43.88	44.19	44.61
0.2569	1.011294	1.008514	1.004933	1.000692	43.48	44.03	44.37	44.73
0.3072	1.012831	1.010030	1.006415	1.002153	43.52	44.06	44.46	44.84
0.3502	1.014140	1.011293	1.007702	1.003401	43.54	44.15	44.44	44.89
0.3934	1.015451	1.012571	1.008934	1.004642	43.56	44.19	44.57	44.96
0.4462	1.017025	1.014122	1.010471	1.006141	43.62	44.23	44.61	45.05
Glycine + 0.2642	: mol·kg ⁻¹ [BMIM]][Ibu] + water						
0.0000	1.005304	1.002425	0.998680	0.994296				
0.1163	1.008928	1.006002	1.002212	0.997801	43.68	44.12	44.56	44.62
0.1545	1.010105	1.007172	1.003361	0.998942	43.72	44.10	44.58	44.70
0.2082	1.011751	1.008781	1.004970	1.000532	43.75	44.22	44.59	44.79
0.2518	1.013085	1.010084	1.006260	1.001816	43.76	44.28	44.64	44.84
0.3115	1.014888	1.011842	1.007997	1.003563	43.81	44.39	44.76	44.90
0.3535	1.016129	1.013093	1.009221	1.004772	43.90	44.38	44.80	44.97
0.4008	1.017569	1.014501	1.010602	1.006141	43.85	44.36	44.80	45.00
0.4472	1.018928	1.015825	1.011921	1.007461	43.93	44.47	44.88	45.06
L-Alanine + wate	уг							
0.0000	0.999094	0.997045	0.994025	0.990190				
0.1005	1.002040	0.999947	0.996874	0.993006	59.63	60.14	60.81	61.33
0.1495	1.003461	1.001352	0.998258	0.994357	59.64	60.11	60.74	61.35
0.2002	1.004921	1.002789	0.999671	0.995754	59.67	60.15	60.77	61.34
0.2489	1.006293	1.004151	1.001018	0.997071	59.77	60.21	60.79	61.40
0.2959	1.007616	1.005441	1.002292	0.998330	59.81	60.30	60.86	61.44
0.3467	1.009014	1.006828	1.003659	0.999670	59.91	60.38	60.93	61.52
0.3960	1.010361	1.008181	1.004968	1.000990	59.99	60.39	61.00	61.51

Table 3 continue	р							
$m/(\text{mol}\cdot\text{kg}^{-1})^{b}$		$10^{-3} d/(1)$	kg·m ^{−3})			$10^{6} V_{\phi}$ /(n	$n^3 \cdot mol^{-1})$	
	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
0.4425	1.011627	1.009420	1.006191	1.002191	60.04	60.47	61.07	61.59
L-Alanine + 0.11	10 mol·kg ⁻¹ [BMIN	M][Ibu] + water						
0.0000	1.001474	0.999110	0.995832	0.991809				
0.0989	1.004327	1.001934	0.998638	0.994589	60.04	60.41	69.09	61.09
0.1511	1.005812	1.003387	1.000083	0.996032	60.07	60.55	60.83	61.15
0.1996	1.007173	1.004728	1.001406	0.997339	60.15	60.63	60.96	61.32
0.2551	1.008722	1.006236	1.002905	0.998826	60.20	60.75	61.07	61.43
0.2970	1.009881	1.007364	1.004021	0.999917	60.23	60.83	61.16	61.57
0.3466	1.011231	1.008677	1.005337	1.001234	60.30	60.93	61.23	61.6
0.3934	1.012524	1.009918	1.006544	1.002423	60.29	60.09	61.35	61.74
0.4459	1.013934	1.011288	1.007853	1.003741	60.35	61.07	61.53	61.88
L-Alanine + 0.180	00 mol·kg ⁻¹ [BMIN	M][Ibu] + water						
0.0000	1.003279	1.000598	0.997203	0.993001				
0660.0	1.006101	1.003408	0.999985	0.995761	60.32	60.53	60.92	61.28
0.1492	1.007513	1.004803	1.001367	0.997145	60.36	60.64	61.02	61.30
0.1969	1.008852	1.006132	1.002670	0.998429	60.35	60.63	61.09	61.43
0.2542	1.010423	1.007686	1.004204	0.999978	60.45	60.76	61.22	61.45
0.2980	1.011611	1.008873	1.005378	1.001122	60.52	60.8	61.25	61.58
0.3561	1.013191	1.010433	1.006901	1.002656	60.54	60.85	61.35	61.62
0.3968	1.014312	1.011526	1.007993	1.003680	60.51	60.86	61.33	61.76
0.4278	1.015152	1.012330	1.008791	1.004480	60.51	60.93	61.38	61.79
L-Alanine + 0.261	02 mol·kg ⁻¹ [BMIN	M][Ibu] + water						
0.0000	1.005193	1.002333	0.998671	0.994245				
0.0993	1.007990	1.005118	1.001432	0.996989	60.58	60.79	61.15	61.47
0.1509	1.009424	1.006536	1.002844	0.998383	60.62	60.90	61.22	61.60

Table 3 continue	þć							
$m/(\text{mol}\cdot\text{kg}^{-1})^{b}$		$10^{-3} d/(1)$	⟨g·m ⁻³)			$10^{6} V_{\phi}$ /(n	$n^3 \cdot mol^{-1})$	
	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
0.1933	1.010601	1.007688	1.003991	0.999538	60.62	60.09	61.29	61.58
0.2549	1.012299	1.009362	1.005641	1.001171	60.61	61.01	61.36	61.69
0.2994	1.013521	1.010545	1.006841	1.002361	60.60	61.08	61.34	61.68
0.3468	1.014794	1.011805	1.008062	1.003556	60.65	61.12	61.48	61.87
0.3959	1.016128	1.013092	1.009361	1.004858	60.63	61.17	61.47	61.82
0.4498	1.017561	1.014479	1.010732	1.006216	60.67	61.26	61.58	61.94
^a Standard uncert	tainties u are $u(T) =$	= 0.01 K, u(p) = 0.01 K	01 MPa and the esti	imated uncertainty <i>i</i>	$u_{\rm c}(V_{\phi}) = 0.06 \times 10$	$^{-6}$ m ³ ·mol ⁻¹		

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^b Relative standard uncertainties u_r for molalities of ionic liquid and amino acids are $u_r(m_{\rm IL}) = 0.02$ and $u_r(m) = 0.005$, respectively, where $m_{\rm IL}$ is the molal concentration of ionic liquid in water and u_r for density is $u_r(d) = 0.001$ kg·m⁻³

volume V_{ϕ}^0 was calculated by least-squares fitting of the apparent molar volume V_{ϕ} by the following equation [43, 44]:

$$V_{\phi} = V_{\phi}^0 + S_V m \tag{2}$$

where S_V is the experimental slope indicating solute–solute interactions and *m* is the molality of the amino acids in water and in the aqueous solutions of [BMIM][Ibu]. The values of V_{ϕ}^0 and S_V , together with their standard deviation $\sigma(V_{\phi})$ derived by least-squares fitting of the V_{ϕ} values with Eq. 2, are reported in Table 4. The V_{ϕ}^0 values increase with increases in the concentration of [BMIM][Ibu] and with temperature. Further, at each temperature, the V_{ϕ}^0 values increase with increase in the chain length of alkyl part in going from glycine to L-alanine.

The temperature dependence of standard partial molar properties provides vital information about solute–solvent interactions, i.e. ion–solvent or zwitterions–ion interactions present in solutions, since solute–solute interactions, like ion–ion or zwitterion–zwitterion interactions at infinite dilution, are negligible. The increase of V_{ϕ}^0 values with the increase in temperature for amino acids can be explained by considering the size of the primary and secondary solvation layers. At higher temperature, the solvent from the secondary hydration layer of solutes is released into the bulk of the solvent, resulting in expansion of the primary hydration layer [45]. From Table 4, it is also observed that the magnitude of S_V is positive for all concentrations of [BMIM][Ibu] in water at all studied temperatures. The positive values of S_V indicate the presence of solute–solute interactions of amino acid in water and in the aqueous solutions of [BMIM][Ibu]. The smaller values of S_V compared to V_{ϕ}^0 suggest that solute–solvent interactions dominate over solute–solute interactions.



Fig. 1 Apparent molar volumes of L-alanine in 0.1800 mol·kg⁻¹ [BMIM][Ibu] + water at the experimental temperatures *T*: (*square*) 288.15 K; (*triangle*) 298.15 K; (*diamond*) 308.15 K; (*circle*) 318.15 K



Fig. 2 Apparent molar volumes of glycine in several concentration of [BMIM][Ibu] in water at T = 298.15 K: (*square*) 0.0000; (*triangle*) 0.1090; (*diamond*) 0.1801; (*circle*) 0.2642 mol·kg⁻¹

The variation of standard partial molar volume V_{ϕ}^{0} with the temperature can be expressed by the following general polynomial equation:

$$V_{\phi}^0 = A + BT + CT^2 \tag{3}$$

where *A*, *B* and *C* have been evaluated by the least-squares fitting of the standard partial molar volumes at experimental temperatures. The standard apparent molar volumes of glycine in water and several concentrations of aqueous [BMIM][Ibu] solutions are plotted versus the experimental temperatures in Fig. 3. The standard apparent molar expansibility were calculated as follows [38]:

$$E^{0}_{\phi} = \left(\frac{\partial V^{0}_{\phi}}{\partial T}\right)_{p} = B + 2CT \tag{4}$$

The standard apparent molar expansibilities originate from two contributions, E_{ϕ}^{0} (elect.) and $E_{\phi}^{0}(\text{str.})$, where $E_{\phi}^{0}(\text{elect.})$ is the standard apparent molar expansibility due to electrostriction changes (contribution of hydration around the solute) whereas $E_{\phi}^{0}(\text{str.})$ denotes the standard apparent molar expansibility that accounts for changes in the solvent's structure. The structural component $E_{\phi}^{0}(\text{str.})$ dominates over $E_{\phi}^{0}(\text{elect.})$ at low temperatures whereas $E_{\phi}^{0}(\text{elect.})$ dominates at the higher temperatures [46]. The calculated values of standard apparent molar expansibility E_{ϕ}^{0} for the investigated solutions are given in Table 4. The E_{ϕ}^{0} values decrease with increase in temperature. This may be attributed to the fact that molecular motions become fast through enhancement in temperature and the difference in water structure between the hydration shell and bulk water becomes smaller; consequently the corresponding effect from the overlap of solvation shells becomes weaker.

Table 4 ¹ Hepler's c	Values of standard app onstant expansion and	parent molar volume, V_{ϕ}^{0} , 1 $(\partial^{2}V_{\phi}^{0}/\partial T^{2})_{p}$ of glycin	experimental e and L-alanin	slope, S_v , transfer volute in water and in aquee	mes $\Delta_{\rm tr} V_{\phi}^0$, standard appare bus solutions of [BMIM][It	nt molar expan bu] at $T = (28)$	sibility, E_{ϕ}^{0} , coefficient of thermal, α , 8.15 to 318.15) K
$T(\mathbf{K})$	$10^6 V_{\phi}^0/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^6 S_\nu/(\mathrm{m}^3 \cdot \mathrm{mol}^{-2} \cdot \mathrm{kg})$	$10^6 \sigma(V_\phi)$	$10^6 \Delta V_{\phi}^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^{6}E_{\phi}^{0}/(\mathrm{m}^{3}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$	$10^3 \alpha ({\rm K}^{-1})$	$10^{6} \left(\widehat{\partial}^{2} V_{\phi}^{0} / \widehat{\partial} T^{2} \right)_{p}^{n} / (\mathrm{m}^{3} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-2})$
Glycine +	· 0 mol·kg ⁻¹ [BMIM]	[Ibu]					
288.15	42.20 ± 0.06	1.70 ± 0.19	0.04	I	0.096	1.641	-0.0018
	42.29 ^a 42.35 ^b						
	42.37 ^c						
298.15	43.23 ± 0.02	1.43 ± 0.08	0.02	1	0.078	1.319	
	43.35 ^d						
	43.24 ^e						
	43.26^{f}						
	43.30^{g}						
308.15	43.58 ± 0.07	1.42 ± 0.23	0.06	Ι	0.060	1.000	
	43.76^{g}						
	43.80^{f}						
	43.79 ^h						
318.15	44.07 ± 0.05	1.08 ± 0.17	0.05	I	0.042	0.698	
	44.14 ⁱ						
	44.17 ^h						
	44.18 ^e						
Glycine +	- 0.1090 mol·kg ⁻¹ [B]	[Ibu][Ibu]					
288.15	42.74 ± 0.02	1.16 ± 0.08	0.02	0.73	0.078	1.826	-0.00110
298.15	43.45 ± 0.02	1.53 ± 0.06	0.02	0.41	0.054	1.232	

Table 4 c	ontinued						
<i>T</i> (K)	$10^6 V_{\phi}^0/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^6 S_{\nu}/(\mathrm{m}^3 \cdot \mathrm{mol}^{-2} \cdot \mathrm{kg})$	$10^6 \sigma(V_\phi)$	$10^6 \Delta V_{\phi}^0/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^{6}E_{\phi}^{0}/(\mathrm{m}^{3}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$	$10^{3} \alpha / (\mathrm{K}^{-1})$	$10^{6} \left(\partial^{2} V_{\phi}^{0} / \partial T^{2} \right)_{p}^{n} / (\mathrm{m}^{3} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-2})$
308.15	43.64 ± 0.02	1.63 ± 0.08	0.02	0.20	0.029	0.663	
318.15	44.09 ± 0.02	1.65 ± 0.06	0.02	0.07	0.005	0.103	
Glycine +	· 0.1801 mol·kg ⁻¹ [BM	[Ibu][Ibu]					
288.15	43.14 ± 0.03	1.14 ± 0.10	0.03	1.13	0.047	1.087	-0.00130
298.15	43.62 ± 0.03	1.44 ± 0.09	0.03	0.58	0.039	0.903	
308.15	44.02 ± 0.03	1.42 ± 0.11	0.04	0.33	0.032	0.726	
318.15	44.24 ± 0.02	1.87 ± 0.07	0.02	0.26	0.024	0.551	
Glycine +	· 0.2642 mol·kg ⁻¹ [BN	[Ibu][Ibu]					
288.15	43.60 ± 0.03	0.72 ± 0.08	0.03	1.59	0.040	0.911	-0.00155
298.15	43.99 ± 0.04	1.08 ± 0.13	0.04	0.95	0.033	0.755	
308.15	44.42 ± 0.03	1.02 ± 0.09	0.03	0.66	0.027	0.604	
318.15	44.50 ± 0.02	1.28 ± 0.06	0.02	0.52	0.020	0.454	
L-Alanine	+ 0 mol·kg ⁻¹ [BMIM	[][Ibu]					
288.15	59.45 ± 0.04	1.61 ± 0.14	0.04	I	0.056	0.944	0.00010
	59.67 ^f						
	59.73 ^a						
	58.96^{h}						
298.15	59.97 ± 0.03 $59.99^{\rm h}$	1.52 ± 0.11	0.03	I	0.057	0.952	

Table 4 c	ontinued						
<i>T</i> (K)	$10^6 V_{\phi}^0/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^6 S_\nu/(\mathrm{m}^3 \cdot \mathrm{mol}^{-2} \cdot \mathrm{kg})$	$10^6 \sigma(V_{\phi})$	$10^6 \Delta V_{\phi}^0/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^{6}E_{\phi}^{0}/(\mathrm{m}^{3}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$	$10^3 \alpha ({\rm K}^{-1})$	$10^{6} \left(\widehat{\partial}^{2} V_{\phi}^{0} / \widehat{\partial} T^{2} \right)_{p}^{n} / (\mathrm{m}^{3} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-2})$
308.15	60.63 ± 0.03 $60.40^{1,j}$ 60.44^{k}	1.58 ± 0.11	0.03	1	0.058	0.959	
	60.88 ^m						
318.15	61.22 ± 0.03	1.29 ± 0.11	0.04	I	0.059	0.967	
	61.31 ¹						
	61.46 ⁱ						
L-Alanine	$+ 0.1110 \text{ mol} \cdot \text{kg}^{-1}$ [F	3MIM][Ibu]					
288.15	59.96 ± 0.01	1.05 ± 0.04	0.01	0.54	0.024	0.400	0.00035
298.15	60.25 ± 0.03	1.89 ± 0.08	0.02	0.22	0.027	0.456	
308.15	60.48 ± 0.03	2.27 ± 0.09	0.02	0.20	0.031	0.512	
318.15	60.85 ± 0.04	2.29 ± 0.10	0.03	0.06	0.034	0.567	
L-Alanine	$+ 0.1800 \text{ mol} \cdot \text{kg}^{-1}$ [F	3MIM][Ibu]					
288.15	60.26 ± 0.04	0.69 ± 0.13	0.04	0.94	0.022	0.362	0.00030
298.15	60.44 ± 0.03	1.14 ± 0.09	0.03	0.39	0.026	0.435	
308.15	60.82 ± 0.03	1.39 ± 0.12	0.04	0.33	0.030	0.506	
318.15	61.09 ± 0.03	1.60 ± 0.11	0.04	0.20	0.035	0.579	
L-Alanine	$+ 0.2602 \text{ mol·kg}^{-1} [\text{F}]$	3MIM][Ibu]					
288.15	60.57 ± 0.02	0.19 ± 0.06	0.02	1.40	0.014	0.227	0.00020
298.15	60.72 ± 0.03	0.96 ± 0.09	0.03	0.76	0.023	0.383	
308.15	61.05 ± 0.03	1.15 ± 0.10	0.03	0.66	0.033	0.536	

<i>T</i> (K)	$10^6 V_{\phi}^0/(\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^6 S_{\nu}/(\mathrm{m}^3 \cdot \mathrm{mol}^{-2} \cdot \mathrm{kg})$	$10^6 \sigma(V_\phi)$	$10^6 \Delta V_{\phi}^0 / (\mathrm{m}^3 \cdot \mathrm{mol}^{-1})$	$10^{6}E_{\phi}^{0}/(\mathrm{m}^{3}\cdot\mathrm{mol}^{-1}\cdot\mathrm{K}^{-1})$	$10^{3} \alpha / (\mathrm{K}^{-1})$	$10^{6} \left(\widehat{\partial}^{2} V_{\phi}^{0} / \widehat{\partial} T^{2} \right)_{p}^{n} / (\mathrm{m}^{3} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-2})$
318.15	61.37 ± 0.04	1.25 ± 0.15	0.05	0.46	0.042	0.688	
^a Reference	e [31]						
b Reference	e [37]						
Keterence	e [33]						
d Reference	e [34]						
e Reference	e [35]						
f Reference	e [36]						
g Reference	e [37]						
h Reference	e [38]						
i Reference	e [39]						
j Reference	e [40]						
k Reference	e [41]						
¹ Reference	e [26]						
m Referenc	ce [42]						
ⁿ The estin	nated uncertainty u _c (1	$10^{6}(\partial^{2}V_{\phi}^{0}/\partial T^{2})_{n}) = 0.00$	009 m ³ ·mol ⁻	$^{1}.K^{-2}$			
^m Referenc ⁿ The estin	ce [42] nated uncertainty u _c (1	$\{0^{6}(\partial^{2}V^{0}_{0}/\partial T^{2})_{}\}=0.00^{6}$	009 m ³ ·mol ⁻	1.K ⁻²			



Fig. 3 Standard partial molar volumes of glycine at several concentration of [BMIM][Ibu] in water: (*square*) 0.0000; (*triangle*) 0.1090; (*diamond*) (0.1801; (*circle*) 0.2642 mol·kg⁻¹ at the experimental temperatures

The values of the standard partial molar volume were used to calculate the coefficient of thermal expansion α according to the following equation [38, 46]:

$$\alpha = \frac{E_{\phi}^0}{V_{\phi}^0} \tag{5}$$

The values of α for the studied solutions are given in Table 4. The coefficient of thermal expansion α is a measure for the response of a system's volume to a change in temperature. A larger value indicates greater sensitivity in the volume change due to a change of temperature.

Hepler [47] developed a general thermodynamic expression to determine the capacity of solute as a structure maker or structure breaker in mixed solvent system using general thermodynamic expression:

$$\left(\partial C_p / \partial p\right)_T = -T \left(\partial^2 V_{\phi}^0 / \partial T^2\right)_p = 2CT \tag{6}$$

The sign of second derivative of the standard partial molar volume with respect to the temperature, $(\partial^2 V_{\phi}^0/\partial T^2)_p$, reflects the structure making or breaking ability of a solute in the solution. If the sign of $(\partial^2 V_{\phi}^0/\partial T^2)_p$ is negative, the solute is a structure breaker [47], otherwise it is a structure maker. The values of $(\partial^2 V_{\phi}^0/\partial T^2)_p$ for the investigated solutions are presented in Table 4. From this table, the negative values of $(\partial^2 V_{\phi}^0/\partial T^2)_p$ for the aqueous solution of glycine demonstrate its structure breaking ability which reduce with increasing concentration of [BMIM][Ibu]. In the aqueous solutions of L-alanine a positive

$^{\mathrm{b}}m \; (\mathrm{mol}\cdot\mathrm{kg}^{-1})$		T = 288.15 K			T = 298.15 K		T_{-}	= 308.15 K			T = 318.15 K	
	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(\mathrm{m}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{Pa}^{-1})}$	Нu	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(m^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})}$	ни	u (m·s ⁻¹)	$\frac{10^{14}}{mol^{-1} \cdot Pa^{-1}}$	ни	и (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(m^3 \cdot mol^{-1} \cdot Pa^{-1})}$	Нu
Glycine + wate												
0.0000	1466.56			1496.91			1520.00			1536.63		
0.1142	1473.00	-3.105	6.03	1502.82	-2.569	5.56	1525.51	-2.247	5.18	1541.86	-2.026	4.79
0.1525	1475.17	-3.099	6.01	1504.76	-2.543	5.51	1527.30	-2.208	5.14	1543.63	-2.017	4.84
0.1962	1477.50	-3.043	5.94	1507.12	-2.565	5.54	1529.37	-2.187	5.12	1545.55	-1.990	4.83
0.2484	1480.28	-2.987	5.87	1509.88	-2.559	5.52	1531.89	-2.178	5.11	1547.91	-1.970	4.82
0.3032	1483.16	-2.938	5.80	1512.78	-2.550	5.51	1534.38	-2.145	5.06	1550.39	-1.956	4.82
0.3537	1485.96	-2.920	5.77	1515.18	-2.496	5.43	1537.03	-2.181	5.10	1552.80	-1.964	4.83
0.4004	1488.47	-2.902	5.74	1517.56	-2.480	5.41	1539.17	-2.149	5.06	1554.90	-1.957	4.82
0.4496	1491.08	-2.875	5.70	1519.96	-2.444	5.35	1541.83	-2.174	5.08	1557.20	-1.951	4.81
Glycine + 0.11i)9 ^b mol·kg ⁻	¹ [BMIM][Ibu] + wat	er									
0.0000	1496.60			1521.89			1540.85			1553.81		
0.1140	1502.47	-2.565	3.39	1527.38	-2.199	3.22	1545.95	-1.921	3.08	1558.75	-1.800	2.99
0.1537	1504.49	-2.544	3.39	1529.23	-2.164	3.23	1547.71	-1.906	3.06	1560.47	-1.791	2.98
0.2080	1507.14	-2.489	3.41	1531.80	-2.143	3.21	1550.15	-1.900	3.05	1562.87	-1.791	2.98
0.2520	1509.30	-2.461	3.38	1533.90	-2.133	3.20	1552.12	-1.886	3.04	1564.69	-1.762	2.95
0.2970	1511.64	-2.462	3.38	1535.89	-2.097	3.16	1554.14	-1.880	3.03	1566.49	-1.728	2.92
0.3499	1514.17	-2.428	3.34	1538.37	-2.078	3.15	1556.34	-1.841	2.99	1568.80	-1.718	2.91
0.3997	1516.54	-2.396	3.31	1540.75	-2.069	3.13	1558.43	-1.814	2.97	1570.87	-1.695	2.89
0.4467	1518.82	-2.378	3.29	1542.82	-2.041	3.11	1560.38	-1.787	2.94	1572.80	-1.680	2.87
Glycine + 0.18)1 mol·kg ⁻¹	[BMIM][Ibu] + wate	r									
0.0000	1510.82			1533.21			1549.33			1560.20		
0.1075	1515.88	-2.187	2.40	1538.09	-1.971	2.31	1554.01	-1.801	2.23	1564.67	-1.664	2.16

Table 5 contin	ned											
^b $m \pmod{\text{kg}^{-1}}$		T = 288.15 K			T = 298.15 K		Τ	= 308.15 K			T = 318.15 K	
	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(m^3 \cdot mol^{-1} \cdot Pa^{-1})}$	Чu	и (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(m^{3} \cdot mol^{-1} \cdot Pa^{-1})}$	ни	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{mol^{-1}\cdot Pa^{-1}})$	Hи	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(\mathrm{m}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{Pa}^{-1})}$	Hu
0.1501	1517.86	-2.168	2.39	1539.98	-1.942	2.29	1555.81	-1.778	2.21	1566.42	-1.641	2.14
0.2013	1520.30	-2.167	2.38	1542.32	-1.943	2.29	1557.94	-1.745	2.19	1568.51	-1.622	2.13
0.2569	1522.90	-2.145	2.37	1544.90	-1.937	2.28	1560.27	-1.715	2.17	1570.77	-1.600	2.11
0.3072	1525.17	-2.118	2.35	1547.12	-1.917	2.27	1562.38	-1.697	2.16	1572.93	-1.602	2.11
0.3502	1527.13	-2.103	2.34	1548.96	-1.888	2.25	1564.29	-1.707	2.16	1574.66	-1.586	2.10
0.3934	1529.12	-2.092	2.33	1550.89	-1.878	2.24	1566.13	-1.691	2.15	1576.24	-1.549	2.07
0.4462	1531.71	-2.097	2.32	1553.13	-1.852	2.22	1568.39	-1.684	2.14	1578.23	-1.519	2.05
Glycine + 0.26	42 mol·kg ⁻¹	[BMIM][Ibu] + wate	зr									
0.0000	1525.19			1544.65			1558.67			1566.95		
0.1163	1530.58	-2.028	1.89	1549.85	-1.843	1.82	1563.37	-1.567	1.70	1571.42	-1.448	1.64
0.1545	1532.35	-2.019	1.88	1551.54	-1.834	1.81	1564.93	-1.564	1.69	1572.94	-1.456	1.64
0.2082	1534.90	-2.027	1.88	1553.94	-1.814	1.80	1567.02	-1.538	1.67	1574.91	-1.417	1.62
0.2518	1537.00	-2.035	1.88	1555.90	-1.809	1.80	1568.94	-1.561	1.69	1576.69	-1.432	1.62
0.3115	1539.77	-2.018	1.87	1558.63	-1.809	1.79	1571.22	-1.519	1.66	1578.83	-1.394	1.60
0.3535	1541.63	-1.989	1.85	1560.50	-1.803	1.79	1572.95	-1.518	1.66	1580.56	-1.404	1.61
0.4008	1543.83	-1.988	1.85	1562.59	-1.796	1.78	1574.93	-1.522	1.66	1582.44	-1.406	1.60
0.4472	1545.98	-1.975	1.84	1564.65	-1.780	1.77	1576.83	-1.513	1.65	1584.25	-1.399	1.60
L-Alanine + wi	uter											
0.1005	1473.60	-3.026	6.88	1503.48	-2.520	6.41	1526.12	-2.097	5.98	1542.12	1.663	5.48
0.1495	1476.94	-2.977	6.80	1506.55	-2.462	6.32	1528.97	-2.049	5.90	1544.73	-1.633	5.43
0.2002	1480.37	-2.934	6.73	1509.85	-2.457	6.31	1531.91	-2.010	5.84	1547.60	-1.661	5.45
0.2489	1483.84	-2.942	6.73	1512.84	-2.407	6.22	1534.79	-1.999	5.81	1550.09	-1.612	5.37
0.2959	1487.16	-2.942	6.71	1515.94	-2.411	6.21	1537.54	-1.981	5.77	1552.64	-1.607	5.35
0.3467	1490.48	-2.884	6.63	1519.14	-2.385	6.17	1540.49	-1.959	5.73	1555.26	-1.575	5.30

Table 5 contin	ned											
^b $m \pmod{\text{kg}^{-1}}$		T = 288.15 K			T = 298.15 K		Τ	= 308.15 K			T = 318.15 K	
	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(m^3 \cdot mol^{-1} \cdot Pa^{-1})}$	Hи	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(\mathrm{m}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{Pa}^{-1})}$	Hи	u (m·s ⁻¹)	$\frac{10^{14}}{mol^{-1} \cdot Pa^{-1}})$	Hи	и (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(\mathrm{m}^3\cdot\mathrm{mol}^{-1}\cdot\mathrm{Pa}^{-1})}$	Чu
0.3960	1493.62	-2.827	6.55	1522.05	-2.340	60.9	1543.24	-1.925	5.67	1558.19	-1.610	5.33
0.4425	1496.24	-2.736	6.43	1525.02	-2.328	6.07	1546.02	-1.920	5.66	1560.74	-1.602	5.31
L-Alanine + 0.	1110 mol kg	⁻¹ [BMIM][Ibu] + wa	ter									
0.0000	1496.93			1522.12			1541.08			1553.97		
0.0989	1503.38	-2.470	3.98	1528.12	-2.123	3.76	1546.73	-1.786	3.52	1559.17	-1.488	3.30
0.1511	1506.72	-2.434	3.94	1531.33	-2.102	3.74	1549.66	-1.752	3.49	1561.89	-1.471	3.28
0.1996	1510.00	-2.463	3.95	1534.32	-2.089	3.72	1552.34	-1.716	3.45	1564.41	-1.447	3.25
0.2551	1513.56	-2.429	3.91	1537.72	-2.066	3.69	1555.42	-1.690	3.43	1567.29	-1.429	3.23
0.297	1516.17	-2.396	3.88	1540.12	-2.021	3.65	1557.68	-1.661	3.40	1569.43	-1.405	3.21
0.3466	1519.33	-2.374	3.85	1543.12	-2.003	3.63	1560.42	-1.646	3.38	1571.85	-1.375	3.17
0.3934	1522.37	-2.365	3.84	1545.89	-1.981	3.60	1562.93	-1.618	3.35	1574.24	-1.356	3.15
0.4459	1525.63	-2.337	3.80	1548.85	-1.942	3.56	1565.80	-1.593	3.32	1576.93	-1.340	3.14
L-Alanine + 0.2	1800 mol kg	⁻¹ [BMIM][Ibu] + wa	ter									
0.0000	1511.14			1533.45			1549.88			1560.91		
0660.0	1517.16	-2.097	2.79	1539.17	-1.828	2.65	1555.20	-1.536	2.51	1565.91	-1.322	2.37
0.1492	1520.22	-2.091	2.78	1542.12	-1.832	2.65	1557.98	-1.553	2.50	1568.42	-1.310	2.36
0.1969	1523.08	-2.073	2.76	1544.90	-1.829	2.64	1560.50	-1.525	2.48	1570.73	-1.273	2.33
0.2542	1526.62	-2.071	2.75	1548.18	-1.802	2.62	1563.63	-1.518	2.47	1573.62	-1.274	2.33
0.2980	1529.32	-2.066	2.74	1550.79	-1.807	2.62	1566.00	-1.512	2.46	1575.73	-1.247	2.31
0.3561	1532.83	-2.052	2.72	1554.20	-1.802	2.61	1569.12	-1.496	2.45	1578.62	-1.241	2.30
0.3968	1535.31	-2.050	2.72	1556.40	-1.773	2.59	1571.20	-1.479	2.43	1580.68	-1.232	2.29
0.4278	1537.26	-2.054	2.71	1558.23	-1.769	2.58	1572.85	-1.470	2.42	1582.23	-1.229	2.28

^b m (mol·kg ⁻¹)		T = 288.15 K			T = 298.15 K		Т	= 308.15 K			T = 318.15 K	
	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(\mathrm{m}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{Pa}^{-1})}$	Нu	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(m^3 \cdot \text{mol}^{-1} \cdot \text{Pa}^{-1})}$	ни	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\mathrm{mol}^{-1}\cdot\mathrm{Pa}^{-1}}$	Hи	<i>u</i> (m·s ⁻¹)	$\frac{10^{14}}{\kappa_{\varphi}(\mathrm{m}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{Pa}^{-1})}$	Ни
L-Alanine + 0	.2602 mol·k	g ⁻¹ [BMIM][Ibu] + wa	ter									
0.0000	1524.38			1544.15			1558.07			1566.70		
0.0993	1530.45	-2.020	2.28	1549.76	-1.677	2.13	1563.32	-1.430	2.02	1571.57	-1.208	1.91
0.1509	1533.56	-1.991	2.26	1552.69	-1.669	2.12	1566.03	-1.415	2.01	1574.14	-1.208	1.91
0.1933	1536.20	-2.008	2.27	1555.08	-1.658	2.11	1568.30	-1.413	2.00	1576.23	-1.206	1.90
0.2549	1539.92	-1.981	2.25	1558.59	-1.656	2.11	1571.53	-1.397	1.99	1579.12	-1.164	1.87
0.2994	1542.78	-2.006	2.25	1561.10	-1.648	2.10	1574.01	-1.418	1.99	1581.53	-1.204	1.89
0.3468	1545.62	-1.982	2.24	1563.83	-1.646	2.09	1576.52	-1.401	1.98	1583.74	-1.164	1.87
0.3959	1548.72	-1.994	2.23	1566.61	-1.636	2.08	1579.01	-1.382	1.97	1586.20	-1.172	1.86
0.4498	1551.90	-1.965	2.21	1569.63	-1.620	2.07	1581.85	-1.368	1.96	1588.77	-1.149	1.85
^a Standard unc	certainties u	are $u(T) = 0.01$ K, the	estimat	ted uncertain	nty $u_{\rm c}(\kappa_{\rm d}) = 0.019 \times$: 10 ⁻¹⁴	m ³ ·mol·Pa ⁻	$^{-1}$ and $u(p) = 0$	101 MI	a		
^b Relative star ionic liquid an	dard uncert: d u_r for spec	ainties u_r for molalities c ed of sound is $u_r(u) = u_r$	of ionic 0.07	liquid and a	umino acids are $u_{\rm r}(m_{\rm IL})$	= 0.0	2 and $u_{\rm r}(m)$	= 0.005, respec	tively,	where $m_{\rm L}$ is	the molal concentration	n of

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value of $(\partial^2 V_{\phi}^0 / \partial T^2)_p$ is seen, which indicates the structure making power of L-alanine and this ability is strengthened in the presence of [BMIM][Ibu].

The partial molar volume of transfer for amino acids from water to the aqueous solutions of [BMIM][Ibu] was calculated by using the following equation [48]:

$$\Delta_{\rm tr} V_{\phi}^0 = V_{\phi}^0(\text{in the aqueous [BMIM][Ibu]}) - V_{\phi}^0(\text{in water})$$
(7)

The calculated values of $\Delta_{\rm tr} V_{\phi}^0$ for investigated solutions reported in Table 4, are all positive and increase with increase in concentration of [BMIM][Ibu] for both amino acids. The observed positive values of $\Delta_{tr}V_{\phi}^{0}$ suggest strong ion-zwitterion interactions of [BMIM][Ibu] with amino acids [49]. AS according to co-sphere overlap model, there is negligible contribution from solute-solute interactions and hence they provide information regarding solute-solvent interactions. The types of interactions that occur between amino acids and [BMIM][Ibu] can be classified as: (i) ion-hydrophilic interactions (between zwitterionic centers of amino acids and polar groups of [BMIM][Ibu]) (ii) hydrophilic-hydrophilic interactions (between polar groups of amino acids and polar groups of [BMIM][Ibu]), (iii) ion-hydrophobic interactions (between zwitterion centers of amino acids and non-polar groups of [BMIM][Ibu]), and (iv) hydrophobic-hydrophobic interactions (between non-polar groups of amino acids and non-polar groups of [BMIM][Ibu]). Ion-hydrophobic and hydrophobic-hydrophobic interactions contribute negatively based on co-sphere overlap model, whereas ion-hydrophilic and hydrophilichydrophilic interactions contribute positively to the $\Delta_{tr}V^0_{\phi}$ values. Therefore, it is concluded that ion-hydrophilic and hydrophilic-hydrophilic interactions between [BMI-M][Ibu] ions and zwitterionic centers of the amino acids are dominant in ternary solutions (amino acids in the aqueous solutions of [BMIM][Ibu]). The partial molar volumes of transfer in glycine solutions are less rather than L-alanine solutions due to its more hydrophobicity [50].

3.2 Ultrasonic Properties

The values of measured speed of sound data for studied systems are reported in Table 5. In Figs. S3 and S4 (in the supporting information) the speed of sound values for glycine and L-alanine in water at T = 298.15, 308.15 and 318.15 K are compared with the values reported in the literature [28, 29, 51]. Speed of sound data in this work are in fairly good agreement with values reported in these references. Based on the speed of sound and density values, the isentropic compressibilities $\kappa_S(Pa^{-1})$ were calculated from the Laplace–Newton equation [52]:

$$\kappa_S = \frac{1}{d \, u^2} \tag{8}$$

The isentropic compressibility is the sum of two contributions, κ_{s1} (solvent intrinsic) and κ_{s2} (solute intrinsic). The κ_{S1} is the isentropic compressibility due to the compression of solvent (water) and κ_{S2} is the compressibility due to the compression of the solvation shell of solute ([BMIM][Ibu] + water).

Hydration numbers from compression $n_{\rm H}$ were calculated using the following relation [53]:

$$n_{\rm H} = \frac{n_1}{n_2} \left(1 - \frac{\kappa_s}{\kappa_{s0}} \right) \tag{9}$$

where n_1 and n_2 are the number of moles of water and solute (amino acid), respectively, and κ_S and κ_{S0} represent the isentropic compressibility of the solutions and the solvent (aqueous solutions of [BMIM][Ibu]), respectively. The calculated values of $n_{\rm H}$ from Eq. 9 for glycine in water and in the aqueous solutions of 0.1090, 0.1801 and 0.2642 mol·kg⁻¹ [BMIM][Ibu], along with $n_{\rm H}$ values for L-alanine in water and in the aqueous solutions of 0.1110, 0.1800 and 0.2602 mol·kg⁻¹ [BMIM][Ibu], are reported in Table 5. Figure 4 shows the values of hydration number for glycine in aqueous solutions with 0.2642 mol·kg⁻¹ [BMIM][Ibu] and L-alanine in the aqueous solutions with 0.2602 mol·kg⁻¹ [BMIM][Ibu] at T = 298.15 K. As can be seen from this figure, in the aqueous solutions of [BMIM][Ibu] with similar molality. the values of $n_{\rm H}$ for L-alanine are larger than for glycine. This result suggests that L-alanine is more strongly hydrated than glycine. The $n_{\rm H}$ values of amino acids decrease with addition of [BMIM][Ibu]. Decrease of the hydration number relates to the fact that, at high concentrations of [BMIM][Ibu], the stronger interactions between amino acids and [BMIM][Ibu] cause the release of water molecules from the hydration layer to the bulk solution.

The apparent molar isentropic compressibility κ_{ϕ} was calculated from the following relation [54]:

$$\kappa_{\phi} = \frac{(\kappa_{S}d_{0} - \kappa_{S0}d)}{mdd_{0}} + \frac{\kappa_{S}M}{d} \tag{10}$$

where *m* is the molality of amino acids in water and in aqueous solutions of [BMIM][Ibu], *M* is the molar mass of the amino acids and d_0 , κ_{s0} , *d* and κ_s are densities and isentropic compressibilities of the solvent (aqueous solutions of [BMIM][Ibu]) and ternary solutions



Fig. 4 Hydration number calculated from Eq. 9 for glycine in aqueous solutions of 0.2642 mol·kg⁻¹ [BMIM][Ibu] with L-alanine in aqueous solutions with 0.2602 mol·kg⁻¹ [BMIM][Ibu] at T = 298.15 K

(amino acids in aqueous solutions of [BMIM][Ibu]). The resulting values of κ_{ϕ} for the studied solutions are listed in Table 5. The values of apparent molar isentropic compressibility of glycine in aqueous solutions with 0.2642 mol·kg⁻¹ [BMIM][Ibu] and L-alanine in aqueous solutions with 0.2602 mol·kg⁻¹ [BMIM][Ibu] at T = 298.15 K are plotted in Fig. 5. The value of limiting apparent molar isentropic compressibility κ_{ϕ}^{0} is often obtained from the extrapolation of the apparent molar isentropic compressibility κ_{ϕ} to infinite dilution using the following linear equation:

$$\kappa_{\phi} = \kappa_{\phi}^0 + S_k m \tag{11}$$

where S_k is the experimental slope due to solute–solute interactions [53]. The obtained values of κ_{ϕ}^0 and S_k for the studied solutions, along with standard deviation $\sigma(\kappa_{\phi})$ at the experimental temperatures, are listed in Table 6. The values of κ_{ϕ}^0 for glycine and L-alanine in water are compared with the values reported in the literature at T = 288.15 and 298.15 K and fairly good agreement is obtained [55, 56].

As solute–solute interactions are absent at infinite dilution, solute–solvent interactions prevail in the solutions. The more negative values of κ_{ϕ}^{0} for the amino acids at low temperature are attributed to the strong attractive interactions between amino acids and water. With an increase in temperature, the κ_{ϕ}^{0} values become less negative, which means that electrostriction is reduced and some water molecules are released back into the bulk solution. Furthermore, the attractive interactions between ions of [BMIM][Ibu] and amino



Fig. 5 Apparent molar isentropic compressibility of glycine (*triangle*) in 0.2642 mol·kg⁻¹ [BMIM][Ibu] + water and L-alanine (*diamond*) in 0.2602 mol·kg⁻¹ [BMIM][Ibu] + water at T = 298.15 K

T (K)	$10^{14} \kappa_{\phi}^{0}$ (m ³ ·mol ⁻¹ ·Pa ⁻¹)	$10^{14}S_k$ (m ³ ·mol ⁻² ·kg·Pa ⁻¹)	$10^{14} \Delta \kappa_{\phi}^{0}$ (m ³ ·msol ⁻¹ ·Pa ⁻¹)	$10^{14}\sigma(\kappa_{\phi})$
Glycine -	+ water			
288.15	-3.187 ± 0.017	0.733 ± 0.058	_	0.019
	-3.495^{a}			
	-3.50 ^b			
298.15	-2.621 ± 0.021	0.345 ± 0.071	_	0.023
	-2.612^{a}			
	-2.64 ^b			
308.15	-2.240 ± 0.022	0.205 ± 0.073	_	0.023
	-2.198^{a}			
	-2.23 ^b			
318.15	-2.040 ± 0.012	0.221 ± 0.039	-	0.012
	-2.156 ^a			
Glycine -	$+ 0.1090 \text{ mol} \cdot \text{kg}^{-1}$ [BN	IIM][Ibu] + water		
288.15	-2.619 ± 0.011	0.555 ± 0.038	0.666	0.012
298.15	-2.240 ± 0.008	0.450 ± 0.026	0.410	0.008
308.15	-1.977 ± 0.012	0.395 ± 0.041	0.263	0.013
318.15	-1.854 ± 0.009	0.389 ± 0.031	0.382	0.010
Glycine -	$+ 0.1801 \text{ mol} \cdot \text{kg}^{-1}$ [BM	IIM][Ibu] + water		
288.15	-2.218 ± 0.009	0.303 ± 0.029	0.969	0.009
298.15	-2.006 ± 0.010	0.325 ± 0.033	0.615	0.010
308.15	-1.822 ± 0.014	0.342 ± 0.048	0.418	0.015
318.15	-1.704 ± 0.011	0.385 ± 0.037	0.536	0.012
Glycine -	$+ 0.2642 \text{ mol} \cdot \text{kg}^{-1}$ [BN	IIM][Ibu] + water		
288.15	-2.055 ± 0.012	0.162 ± 0.041	1.132	0.013
298.15	-1.860 ± 0.006	0.170 ± 0.018	0.763	0.006
308.15	-1.586 ± 0.011	0.174 ± 0.037	0.654	0.011
318.15	-1.467 ± 0.013	0.168 ± 0.042	0.773	0.013
L-Alanine	e + water			
288.15	-3.103 ± 0.032	0.713 ± 0.110	-	0.035
	-3.086^{a}			
	-3.06 ^b			
298.15	-2.557 ± 0.013	0.527 ± 0.044	-	0.014
	-2.460^{a}			
	-2.42^{b}			
308.15	-2.127 ± 0.012	0.494 ± 0.099	-	0.012
	-2.123^{a}			
	-2.23 ^b			
318.15	-1.674 ± 0.019	0.196 ± 0.065	-	0.021
L-Alanine	$e + 0.1110 \text{ mol} \cdot \text{kg}^{-1}$ [E	BMIM][Ibu] + water		
288.15	-2.532 ± 0.017	0.405 ± 0.045	0.571	0.014
298.15	-2.171 ± 0.014	0.518 ± 0.036	0.386	0.011

Table 6 Values of partial molar isentropic compressibility (κ_{ϕ}^0) , experimental slope (S_k) , partial molar isentropic compressibility of transfer $(\Delta \kappa_{\phi}^0)$ for glycine and L-alanine in water and in the aqueous solutions of [BMIM][Ibu] at T = (288.15 to 318.15) K

Table 6 continued

T (K)	$10^{14} \kappa_{\phi}^{0}$ (m ³ ·mol ⁻¹ ·Pa ⁻¹)	$10^{14}S_k$ (m ³ ·mol ⁻² ·kg·Pa ⁻¹)	$10^{14} \Delta \kappa_{\phi}^{0}$ (m ³ ·msol ⁻¹ ·Pa ⁻¹)	$10^{14}\sigma(\kappa_{\phi})$
308.15	-1.822 ± 0.006	0.528 ± 0.017	0.305	0.005
318.15	-1.537 ± 0.006	0.449 ± 0.015	0.137	0.005
L-Alanine	$+ 0.1800 \text{ mol} \cdot \text{kg}^{-1}$ [BMI	M][Ibu] + water		
288.15	-2.119 ± 0.005	0.164 ± 0.018	0.984	0.006
298.15	-1.853 ± 0.010	0.185 ± 0.032	0.704	0.010
308.15	-1.568 ± 0.009	0.220 ± 0.030	0.559	0.009
318.15	-1.345 ± 0.009	0.288 ± 0.030	0.329	0.009
L-Alanine	$+ 0.2602 \text{ mol} \cdot \text{kg}^{-1}$ [BMI	M][Ibu] + water)		
288.15	-2.022 ± 0.012	0.104 ± 0.041	1.081	0.013
298.15	-1.686 ± 0.007	0.136 ± 0.022	0.878	0.007
308.15	-1.444 ± 0.009	0.148 ± 0.032	0.683	0.010
318.15	-1.229 ± 0.014	0.164 ± 0.047	0.445	0.015

^a Reference [55]

^b Reference [56]

acid molecules induce the dehydration of amino acids at high concentrations of [BMI-M][Ibu] in water, therefore the water molecules around the amino acids are more compressible than those at lower [BMIM][Ibu] concentrations [57].

Partial molar isentropic compressibilities of transfer $\Delta_{tr} \kappa_{\phi}^{0}$ from water to the aqueous solutions of [BMIM][Ibu] have been calculated using the following expression [58]:

$$\Delta_{\rm tr}\kappa_{\phi}^{0} = \kappa_{\phi}^{0}(\text{in aqueous solution of [BMIM][Ibu]}) - \kappa_{\phi}^{0}(\text{in water})$$
(12)

The values of $\Delta_{tr}\kappa_{\phi}^{0}$ for the investigated solutions are presented in Table 6. Positive $\Delta_{tr}\kappa_{\phi}^{0}$ values increase with increasing concentration of [BMIM][Ibu]. The more positive values of κ_{ϕ}^{0} for glycine indicate dominance of the charged end groups NH₃⁺ and COO⁻. The interactions between [BMIM][Ibu] and the zwitterionic centers of amino acids increase with increasing [BMIM][Ibu] concentration. As a result, the layer around the solute is much more compressible than bulk water and leads to an increase in the compressibility with increase in [BMIM][Ibu] concentration. Positive $\Delta_{tr}\kappa_{\phi}^{0}$ values for the amino acids are similar to the behavior observed for the partial molar volume of transfer, which supports our analysis of volumetric data.

3.3 Pair and Triplet Interaction Coefficients

The McMillan and Mayer [59] theory, which was further discussed by Friedman and Krishnan [60], presents a formalism to calculate the interaction coefficients, which permits the separation of effects due to interactions between pairs of solute molecules and those due to its interactions between more than two solute molecules. Thus, the partial molar

volume of transfer and partial molar isentropic compressibility of transfer can be expressed as follows:

$$\Delta_{\rm tr} V_{\phi}^0 = 2V_{\rm AB} \, m_{\rm B} \, + 3 \, V_{\rm ABB} \, m_{\rm B}^2 + \dots \tag{13}$$

$$\Delta_{\rm tr}\kappa_{\phi}^0 = 2\kappa_{\rm AB}\,m_{\rm B} + 3\,\kappa_{\rm ABB}\,m_{\rm B}^2 + \dots \tag{14}$$

where A denotes amino acids, B denotes [BMIM][Ibu] and $m_{\rm B}$ is the molality of amino acids in the aqueous solutions of [BMIM][Ibu]. The corresponding parameters $V_{\rm AB}$ and $V_{\rm ABB}$ for volume and $\kappa_{\rm AB}$ and $\kappa_{\rm ABB}$ for isentropic compressibility denote pair-interaction and triplet-interaction coefficients. These constants were calculated by fitting of the $\Delta_{\rm tr} V_{\phi}^0$ and $\Delta_{\rm tr} \kappa_{\phi}^0$ values to the above equations and are reported in Table 7. The pair-interaction coefficients $V_{\rm AB}$ and $\kappa_{\rm AB}$ are positive, whereas the triplet-interaction coefficients $V_{\rm ABB}$ and $\kappa_{\rm ABB}$ are negative for glycine and L-alanine at all temperatures. The positive values of $V_{\rm AB}$ and $\kappa_{\rm AB}$ indicate that the dominant interactions are mainly pairwise. These values decrease with increase in temperature in all cases under study [61].

3.4 Viscosity B Coefficients

The experimental viscosities η of glycine in water and in the aqueous solutions of 0.1090, 0.1801 and 0.2642 mol·kg⁻¹ [BMIM][Ibu], along with viscosity values for L-alanine in water and in the aqueous solutions of 0.1110, 0.1800 and 0.2602 mol·kg⁻¹ [BMIM][Ibu], are reported in Table 8. The viscosity data of (glycine + water) and (L-alanine + water) at the experimental temperatures are in fairly good agreement with the literature values (Figs. S5 and S6 in supporting information) [18, 62, 63]. Figure 6 shows the viscosity values of (L-alanine + [BMIM][Ibu] + water) solutions with 0.0000, 0.1110, 0.1800 and 0.2602 mol·kg⁻¹ [BMIM][Ibu] + water at T = 298.15 K. The viscosity increases with an increase in the molar mass of amino acids, i.e. from glycine to L-alanine. The viscosity values have been found to increase with increase in concentration of amino acids as well as

System	For volume		For compression	
	$\frac{10^6 V_{AB}}{(m^3 \cdot mol^{-2} \cdot kg)}$	$\frac{10^{6}V_{ABB}}{(m^{3}\cdot mol^{-3}\cdot kg^{2})}$	$\frac{10^{14} \kappa_{AB}}{(m^3 \cdot mol^{-2} \cdot kg \cdot Pa^{-1})}$	$\frac{10^{14}\Delta\kappa_{AB}}{(m^3 \cdot mol^{-3} \cdot kg^2 \cdot Pa^{-1})}$
Glycine +	[BMIM][Ibu] + wate	r		
288.15	3.12	-1.91	2.76	-1.60
298.15	1.57	-0.97	1.80	-1.07
308.15	1.35	-0.81	1.43	-0.87
318.15	0.92	-0.60	1.23	-0.76
L-Alanine -	+ [BMIM][Ibu] + wa	ter		
288.15	4.44	-4.55	3.55	-3.82
298.15	3.03	-2.93	2.21	-1.53
308.15	1.16	0.60	1.78	-1.33
318.15	-0.16	2.68	0.76	0.09

Table 7 Pair (V_{AB} and κ_{AB}) and triplet (V_{ABB} and κ_{ABB}) interaction coefficients for glycine and L-alanine in water and in aqueous solutions of [BMIM][Ibu] at T = 288.15–318.15 K

(77) = 7 are since	1 (CT.01C M CT.C								
$m^{\rm a} \; ({\rm mol}\cdot {\rm kg}^{-1})$		μ (ml	Pa·s)		$m \pmod{\text{kg}^{-1}}$		μ (mł	Pa·s)	
	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
Glycine + water					L-Alanine + wa	ater			
0.0000	1.130	0.888	0.720	0.607	0.0000	1.130	0.888	0.720	0.607
0.1142	1.146	0.899	0.730	0.616	0.1005	1.160	606.0	0.738	0.616
0.1525	1.152	0.904	0.734	0.620	0.1495	1.175	0.921	0.747	0.622
0.1962	1.159	0.910	0.739	0.624	0.2002	1.191	0.933	0.756	0.629
0.2484	1.168	0.917	0.744	0.630	0.2489	1.206	0.945	0.765	0.638
0.3032	1.177	0.924	0.750	0.637	0.2959	1.222	0.955	0.773	0.646
0.3537	1.184	0.931	0.755	0.644	0.3467	1.237	0.966	0.782	0.657
0.4004	1.192	0.937	0.760	0.650	0.396	1.253	0.977	0.791	0.667
0.4496	1.200	0.943	0.765	0.657	0.4425	1.268	0.987	0.799	0.677
Glycine + 0.109	0 ^a mol·kg ⁻¹ [BN	4IIM][Ibu] + water	r		L-Alanine + 0.1	1110 mol·kg ⁻¹ [B	MIM][Ibu] + wa	ter	
0.0000	1.293	0.996	0.798	0.663	0.0000	1.295	1.002	0.806	0.670
0.1140	1.307	1.011	0.808	0.673	0.0989	1.326	1.026	0.824	0.684
0.1537	1.314	1.018	0.814	0.677	0.1511	1.347	1.041	0.836	0.693
0.2080	1.325	1.028	0.822	0.683	0.1996	1.366	1.055	0.848	0.701
0.2520	1.333	1.034	0.828	0.688	0.2551	1.385	1.070	0.860	0.712
0.2970	1.342	1.041	0.834	0.693	0.297	1.403	1.084	0.869	0.718
0.3499	1.351	1.049	0.841	0.699	0.3466	1.419	1.097	0.880	0.726
0.3997	1.360	1.057	0.849	0.705	0.3934	1.436	1.110	0.891	0.733
0.4467	1.368	1.064	0.856	0.711	0.4459	1.456	1.125	0.901	0.742
Glycine + 0.180	1 mol·kg ⁻¹ [BM	IM][Ibu] + water			L-Alanine + 0.1	1800 mol·kg ⁻¹ [B	MIM][Ibu] + wa	ter	
0.0000	1.464	1.131	0.903	0.743	0.0000	1.472	1.138	0.911	0.756
0.1075	1.484	1.144	0.916	0.750	0660.0	1.510	1.166	0.937	0.773
0.1501	1.494	1.152	0.922	0.757	0.1492	1.533	1.183	0.949	0.782

	nuu								
$m^{\rm a} \; ({\rm mol} \cdot {\rm kg}^{-1})$		μ (m	Pa·s)		$m \; (\text{mol·kg}^{-1})$		μ (m)	Pa·s)	
	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
0.2013	1.506	1.162	0.929	0.765	0.1969	1.552	1.196	0.959	0.791
0.2569	1.518	1.173	0.938	0.773	0.2542	1.576	1.213	0.970	0.801
0.3072	1.528	1.182	0.945	0.780	0.2980	1.595	1.228	0.980	0.809
0.3502	1.538	1.190	0.952	0.786	0.3561	1.620	1.247	0.993	0.822
0.3934	1.548	1.198	0.959	0.792	0.3968	1.640	1.259	1.003	0.829
0.4462	1.558	1.207	0.967	0.799	0.4278	1.655	1.270	1.010	0.835
Glycine $+ 0.2$	642 mol·kg ⁻¹ [BM	[IM][Ibu] + water	•		L-Alanine + 0.2	3602 mol·kg ⁻¹ [B	[MIM][Ibu] + wa	ter	
0.0000	1.712	1.315	1.045	0.851	0.0000	1.693	1.304	1.037	0.853
0.1163	1.733	1.332	1.059	0.867	0.0993	1.738	1.334	1.058	0.869
0.1545	1.745	1.340	1.066	0.872	0.1509	1.763	1.352	1.073	0.879
0.2082	1.760	1.352	1.075	0.880	0.1933	1.784	1.367	1.085	0.888
0.2518	1.772	1.362	1.082	0.886	0.2549	1.813	1.389	1.102	0.901
0.3115	1.787	1.375	1.093	0.895	0.2994	1.836	1.409	1.117	0.910
0.3535	1.799	1.384	1.101	0.901	0.3468	1.860	1.427	1.131	0.920
0.4008	1.813	1.395	1.110	0.908	0.3959	1.884	1.444	1.144	0.931
0.4472	1.826	1.405	1.119	0.915	0.4498	1.910	1.463	1.158	0.943
Standard uncer	rtainties u are $u(T)$	$= 0.01$ K, $u(\eta) =$	= 0.005 mPa·s and	u(p) = 0.01 MP.	a				

^a Relative standard uncertainties u_r for molalities of ionic liquid and amino acids are $u_i(m_{1L}) = 0.02$ and $u_r(m) = 0.005$, respectively, where m_{1L} is the molal concentration of ionic liquid in water

an increase in the concentration of [BMIM][Ibu] in the aqueous solutions. This may be attributed to an increase in the solute–solvent (zwitterion–ion) interactions with increase in the number of zwitterions in solutions, which may in turn cause more frictional resistance to the flow of solutions. The viscosity values decrease with an increase in temperature. An increase in temperature increases the kinetic energy of the molecules, resulting in reduced solute–solvent interactions in solution. Due to the increase in the random motion at higher temperatures, the forces of attraction intrinsically decrease and molecules and ions rapidly move of into the empty sites. Such a decrease in interactions seems to be responsible for the decrease in viscosity with an increase in temperature [61–63].

The variation of relative viscosity η_r of amino acids in water and in the aqueous solutions of [BMIM][Ibu] can be represented by the Jones–Dole equation [64]:

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \tag{15}$$

The A coefficient (also called Falkenhagen coefficient, reflecting electrostatic solutesolute interactions) can be calculated theoretically but is zero [65]. Generally, the viscosity B coefficients reflect solute-solvent interactions. In fact, when A coefficients are neglected in Eq. 15, this equation is equivalent to the viscosity equation:

$$\frac{\eta}{\eta_0} = 1 + Bc \tag{16}$$

where η and η_0 are the viscosity of solutions (amino acids in the aqueous solution of [BMIM][Ibu]) and solvent (aqueous solution of [BMIM][Ibu]), respectively, and *c* is the molar concentration of amino acid in the aqueous solution of [BMIM][Ibu]. The viscosity *B* coefficients were obtained from the slope of linear plot of $(\eta/\eta_0 - 1)$ versus *c* by the



Fig. 6 Viscosities of (L-alanine + [BMIM][Ibu] + water) solutions with several concentration of ([BMIM][Ibu] + water) at T = 298.15 K: (*square*) 0.0000; (*triangle*) 0.1110; (*diamond* 0.1800; (*circle*) 0.2602 mol·kg⁻¹

least-squares method. The calculated viscosity *B* coefficients and $\sigma(\eta)$ from fitting the experimental viscosity data with the Jones–Dole equation are given in Table 9.

The viscosity *B* coefficient is a measure of the size, shape and charge of solute molecules as well as the structural effects induced by solute–solvent interactions [66]. Our *B* values at different temperatures were compared with the corresponding data reported in references and again good agreement is obtained [67, 68]. The viscosity *B* coefficient is a tool that provides information about solvation of the solute in solution and the effect on the structure of the solvent in the vicinity of solute molecules. It reflects the net structural effects of the charged end groups and hydrophilic and hydrophobic groups on the solvent molecules. The higher positive values of the viscosity *B* coefficients in the case of Lalanine, as compared to glycine, predict that L-alanine has a greater kosmotropic effect in the aqueous solutions of [BMIM][Ibu], which further suggests more solute–solvent interactions in the case of L-alanine. This is due to the fact that, in the case of glycine, the ion–hydrophilic group interactions between the (COO⁻/NH₃⁺) zwitterionic centers of glycine and ions of [BMIM][Ibu] are higher in comparison to L-alanine [68].

The viscosity *B* coefficients of transfer $\Delta_{tr}B$ from water to the aqueous [BMIM][Ibu] solutions have been calculated as follows [69]:

$\Delta_{tr}B = B$ coefficients in (aqueous solutions of [BMIM][Ibu])-B coefficients(in water)

The calculated values of $\Delta_{tr}B$ for studied solutions are presented in Table 9. The viscosity *B* coefficients for the studied amino acids in the aqueous solutions of [BMIM][Ibu] are higher than the values in water, which results in positive values. The partial molar volume of transfer values decrease with an increase in concentration of [BMIM][Ibu]. The magnitude of the $\Delta_{tr}B$ values is greater in the case of L-alanine as compared to glycine, again suggesting the greater dehydrating effect of glycine. In the case of glycine, the values increase with temperature, which may be due to its more hydrophilic character as compared to L-alanine, having hydrophobic CH₂ groups, and this increase is greater at higher temperatures.

The viscosity data were analyzed on the basis of transition state treatment of relative viscosity of suggested by Feakins and co-workers [70]. The viscosity B coefficient in terms of this theory is given by following equation:

$$B = (\bar{V}_1^0 - \bar{V}_2^0) + \bar{V}_1^0 \left(\frac{\Delta \mu_2^{0*} - \Delta \mu_1^{0*}}{RT}\right)$$
(17)

where $\left(\bar{V}_{1}^{0} = \sum_{i} \frac{x_{i}M_{i}}{\rho}\right)$ is the mean volume of the solvent and $(\bar{V}_{2}^{0} = V_{\phi}^{0})$ is the standard partial molar volume of the pure solute. The \bar{V}_{1}^{0} is the molar volume of the pure solvent. The terms x_{i} and M_{i} denote the mole fractions and molar masses of solvent, and d is the density of the solvent (aqueous solutions of [BMIM][Ibu]) [70]. The Gibbs energies of activation per mole of the solvent, $\Delta \mu_{1}^{0*}$ and $\Delta \mu_{2}^{0*}$, were calculated according to Eyring's simple model by following equations and are listed in Table 9.

$$\Delta \mu_1^{0*} = \Delta G_1^{0*} = RT \ln\left(\frac{\eta_1 V_1^0}{hN_A}\right)$$
(18)

$$\Delta \mu_2^{0*} = \Delta G_2^{0*} = \frac{RT}{V_1^0} \left[B - \left(\bar{V}_1^0 - \bar{V}_2^0 \right) \right]$$
(19)

where *h* is the Planck constant, N_A is the Avogadro number, η_0 is the viscosity of the solvent, and the other symbols have their usual meanings. The values of $\Delta \mu_1^{0*}$ and $\Delta \mu_2^{0*}$ are

Table 9 glycine ar	Values of viscosity nd L-alanine in wat	/ B-coefficients, Gibb ter and aqueous solut	s energy of activatior ions of [BMIM][Ibu]	t per mole of solvent (at $T = 288.15-318.1$	$\Delta \mu_1^{0*}$) and of the sc 5 K	blute $(\Delta \mu_2^{0*})$, and visc	osity B-coefficients c	of transfer $(\Delta_{tr}B)$ for
$T(\mathbf{K})$	$B (\mathrm{dm}^3 \cdot \mathrm{mol}^{-1})$	$\Delta \mu_1^{0*}$ (kJ·mol ⁻¹)	$\Delta \mu_2^{0*}$ (kJ·mol ⁻¹)	$\Delta_{ m tr} B ~({ m dm}^3 \cdot { m mol}^{-1})$	$B \ (dm^3 \cdot mol^{-1})$	$\Delta \mu_1^{0*}$ (kJ·mol ⁻¹)	$\Delta \mu_2^{0*}$ (kJ·mol ⁻¹)	$\Delta_{\rm tr} B ~({\rm dm}^3 \cdot { m mol}^{-1})$
Glycine +	water				L-Alanine + water			
288.15	0.133 ± 0.001	I	I	I	0.277 ± 0.001	I	I	I
	$0.132^{a}, 0.129^{b}$				$0.269^{a}, 0.259^{b}$			
298.15	0.135 ± 0.001	I	I	I	0.258 ± 0.003	I	I	I
	$0.142^{\rm a}, 0.1427^{\rm b}$				$0.258^{a}, 0.253^{b}$			
308.15	0.138 ± 0.001	I	I	I	0.246 ± 0.001	I	I	I
	$0.146^{\rm a}, 0.148^{\rm b}$				$0.250^{a}0.247^{b}$			
318.15	0.166 ± 0.005	I	I	I	0.237 ± 0.011	I	I	I
	$0.150^{a}, 0.152^{b}$				0.2771 ^a			
Glycine +	0.1109 mol·kg ⁻¹ [BI	MIM][Ibu] + water			L-Alanine + 0.1110) mol·kg ⁻¹ [BMIM][Ibu	ı] + water	
288.15	0.149 ± 0.010	9.81	32.17	0.016	0.289 ± 0.003	9.82	52.45	0.012
298.15	0.152 ± 0.002	9.52	33.11	0.017	0.272 ± 0.002	9.54	51.41	0.014
308.15	0.156 ± 0.002	9.28	34.09	0.018	0.265 ± 0.003	9.31	51.40	0.019
318.15	0.172 ± 0.002	60.6	36.90	0.020	0.252 ± 0.003	9.13	50.60	0.023
Glycine +	0.1801 mol·kg ⁻¹ [BM	dIIM][Ibu] + water			L-Alanine + 0.1801	mol·kg ⁻¹ [BMIM][Ibu	ı] + water	
288.15	0.143 ± 0.001	10.19	31.16	0.010	0.283 ± 0.003	10.20	50.90	0.006
298.15	0.147 ± 0.001	9.91	32.08	0.012	0.267 ± 0.003	9.93	49.83	0.009
308.15	0.155 ± 0.002	9.67	33.60	0.017	0.257 ± 0.003	9.70	49.50	0.011
318.15	0.163 ± 0.003	9.48	35.28	0.016	0.243 ± 0.003	9.53	48.53	0.014
Glycine +	0.2642 mol·kg ⁻¹ [BM	MIM][Ibu] + water			L-Alanine + 0.2602	2 mol·kg ⁻¹ [BMIM][Ibu	ı] + water	
288.15	0.142 ± 0.001	10.63	30.94	0.009	0.281 ± 0.001	10.60	50.08	0.004
298.15	0.147 ± 0.001	10.35	31.91	0.012	0.266 ± 0.003	10.32	49.20	0.008
308.15	0.151 ± 0.002	10.12	32.83	0.013	0.256 ± 0.003	10.09	48.80	0.01
318.15	0.163 ± 0.001	9.92	33.50	0.020	0.240 ± 0.002	9.91	47.56	0.011
^a Referen	ice [67]							
^b Referen	ice [68]							

Table 10 alanine + [Values of refi BMIM][Ibu]	ractive indice + water) sol	as (n_D) and molar relations at $T = 288.1$	fractions (R _D) of bi 5-318.15 K	nary (glycine + wat	er), (L-alanine + w	ater) and ternary (₈	glycine + [BMIM]	[Ibu] + water), (L-
m ^a (mol·kg	-1)		^u	D			$10^{6}R_{\rm D}$ (1	n^{3} .mol ⁻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 = 3188.15 K
Glycine +	water								
0.0000	1.3328	1.3322	1.3314	1.3302					
0.1011	1.3342	1.3336	1.3329	1.3318	3.8253	3.8273	3.8317		3.8352
0.1422	1.3347	1.3340	1.3334	1.3323	3.8408	3.8419	3.8475		3.8511
0.1964	1.3353	1.3346	1.3340	1.3329	3.8546	3.8559	3.8617		3.8651
0.2486	1.3359	1.3352	1.3346	1.3335	3.8692	3.8707	3.8766		3.8802
0.3032	1.3366	1.3358	1.3352	1.3342	3.8824	3.8832	3.8890		3.8939
0.3532	1.3372	1.3365	1.3357	1.3348	3.8952	3.8971	3.9007		3.9067
0.4003	1.3377	1.3371	1.3363	1.3354	3.9081	3.9112	3.9150		3.9208
0.4498	1.3383	1.3377	1.3369	1.3360	3.9221	3.9255	3.9293		3.9352
Glycine +	0.1109 ^a mol	kg ⁻¹ [BMIM	[][Ibu] + water						
0.0000	1.3408	1.3396	1.3380	1.3369					
0.1140	1.3405	1.3397	1.3386	1.3372	3.9098	3.9110	3.9124		3.9137
0.1537	1.3411	1.3402	1.3392	1.3378	3.9199	3.9201	3.9226		3.9239
0.2080	1.3419	1.3410	1.3399	1.3385	3.9334	3.9338	3.9353		3.9367
0.2520	1.3425	1.3415	1.3405	1.3391	3.9439	3.9434	3.9461		3.9474
0.297	1.3432	1.3421	1.3412	1.3398	3.9555	3.9541	3.9579		3.9593
0.3499	1.3439	1.3428	1.3419	1.3405	3.9679	3.9667	3.9706		3.9721
0.3997	1.3446	1.3434	1.3425	1.3411	3.9800	3.9780	3.9820		3.9836
0.4467	1.3453	1.3440	1.3431	1.3417	3.9919	3.9890	3.9931		3.9947
Glycine + 1	0.1801 mol·k	[BMIM]	[[Ibu] + water						
0.0000	1.3452	1.3447	1.3427	1.3416					
0.1075	1.3459	1.3450	1.3441	1.3428	4.0936	4.0949	4.0997		4.1029
0.1501	1.3465	1.3456	1.3446	1.3434	4.1042	4.1057	4.1094		4.1138

m ^a (mol·kg	-1)		u	q			$10^{6}R_{\rm D}$ (f)	n^{3} .mol ⁻¹)	
	L	$^{-}$ = 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 = 3188.15 K
0.2013	1.3472	1.3463	1.3452	1.3440	4.1168	4.1184	4.1211		4.1256
0.2569	1.3479	1.3470	1.3460	1.3447	4.1299	4.1316	4.1355		4.1390
0.3072	1.3486	1.3476	1.3466	1.3454	4.1424	4.1432	4.1472		4.1519
0.3502	1.3492	1.3482	1.3471	1.3459	4.1532	4.1541	4.1570		4.1618
0.3934	1.3498	1.3488	1.3477	1.3465	4.1639	4.1650	4.1681		4.1729
0.4462	1.3505	1.3495	1.3484	1.3471	4.1768	4.1780	4.1812		4.1850
Glycine + (0.2642 m	ol·kg ⁻¹ [BMIM]	[Ibu] + water						
0.0000	1.3504	1.3500	1.3480	1.3467					
0.1163	1.3527	1.3517	1.3503	1.3486	4.3084	4.3099	4.3106		4.3107
0.1545	1.3531	1.3522	1.3507	1.3491	4.3167	4.3193	4.3191		4.3204
0.2082	1.3538	1.3529	1.3514	1.3498	4.3300	4.3328	4.3325		4.3339
0.2518	1.3543	1.3534	1.3520	1.3504	4.3400	4.3429	4.3438		4.3452
0.3115	1.3550	1.3541	1.3528	1.3512	4.3539	4.3570	4.3592		4.3606
0.3535	1.3555	1.3546	1.3533	1.3517	4.3639	4.3670	4.3693		4.3707
0.4008	1.3561	1.3551	1.3539	1.3523	4.3753	4.3774	4.3810		4.3825
0.4472	1.3566	1.3557	1.3544	1.3530	4.3858	4.3892	4.3916		4.3953
L-Alanine +	- water								
0.0000	1.3328	1.3322	1.3314	1.3302					
0.1103	1.3341	1.3336	1.3327	1.3317	3.7322	3.7350	3.7374		3.7417
0.1485	1.3346	1.3340	1.3332	1.3322	3.7448	3.7467	3.7502		3.7545
0.2062	1.3354	1.3347	1.3340	1.3329	3.7608	3.7618	3.7665		3.7698
0.2519	1.3360	1.3353	1.3347	1.3335	3.7745	3.7756	3.7813		3.7837
0.2999	1.3366	1.3359	1.3353	1.3342	3.7879	3.7891	3.7949		3.7984
0.3567	1.3373	1.3366	1.3360	1.3350	3.8029	3.8042	3.8101		3.8146

Table 10 continued

Table 10	continued								
m ^a (mol·kg	(-1)		u	Q			$10^6 R_{\rm D}$ (n	n ³ .mol ⁻¹)	
	T = 2	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 = 3188.15 K
0.4121	1.3380	1.3373	1.3367	1.3357	3.8179	3.8194	3.8253		3.8297
0.4525	1.3386	1.3378	1.3372	1.3362	3.8314	3.8320	3.8378		3.8425
L-Alanine ⊣	+ 0.1110 mol	kg ⁻¹ [BMIN.	[][Ibu] + water						
0.0000	1.3404	1.3398	1.3382	1.3337					
0.0989	1.3405	1.3399	1.3389	1.3373	3.9163	3.9185	3.9201		3.9186
0.1511	1.3413	1.3406	1.3396	1.3381	3.9357	3.9370	3.9386		3.9383
0.1996	1.3421	1.3413	1.3403	1.3388	3.9515	3.9520	3.9538		3.9534
0.2551	1.3429	1.3421	1.3411	1.3397	3.9688	3.9694	3.9714		3.9721
0.2970	1.3435	1.3427	1.3417	1.3404	3.9800	3.9811	3.9830		3.9850
0.3466	1.3442	1.3434	1.3424	1.3412	3.9944	3.9954	3.9972		4.0004
0.3934	1.3449	1.3441	1.3431	1.3419	4.0086	4.0098	4.0118		4.0148
0.4459	1.3456	1.3449	1.3438	1.3428	4.0245	4.0271	4.0280		4.0332
L-Alanine ⊣	+ 0.1800 mol-	kg ⁻¹ [BMIN.	[][Ibu] + water						
0.0000	1.3452	1.3447	1.3426	1.3415					
0660.0	1.3469	1.3459	1.3446	1.3437	4.1100	4.1103	4.1104		4.1181
0.1492	1.3475	1.3465	1.3453	1.3443	4.1249	4.1253	4.1265		4.1331
0.1969	1.3481	1.3470	1.3459	1.3449	4.1393	4.1387	4.1411		4.1478
0.2542	1.3487	1.3477	1.3466	1.3456	4.1555	4.1561	4.1585		4.1652
0.2980	1.3492	1.3483	1.3472	1.3461	4.1684	4.1700	4.1726		4.1783
0.3561	1.3500	1.3490	1.3479	1.3468	4.1868	4.1875	4.1902		4.1959
0.3968	1.3505	1.3496	1.3484	1.3473	4.1991	4.2009	4.2025		4.2086
0.4278	1.3509	1.3500	1.3488	1.3477	4.2086	4.2106	4.2123		4.2183

m ^a (mol·kg	-1)		¹ u	0			$10^{6}R_{\rm D}$ (1	m ³ .mol ⁻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 = 3188.15 K
L-Alanine +	- 0.2602	: mol·kg ⁻¹ [BMI	[M][Ibu] + water						
0.0000	1.350	3 1.3495	1.3478	1.3466					
0.0993	1.352	3 1.3512	1.3502	1.3489	4.2896	4.2898	4.2945		4.2992
0.1509	1.353() 1.3520	1.3508	1.3495	4.3063	4.3077	4.3102		4.3150
0.1933	1.353(5 1.3526	1.3514	1.3501	4.3203	4.3219	4.3244		4.3292
0.2549	1.354_{4}	4 1.3534	1.3522	1.3509	4.3399	4.3415	4.3442		4.3491
0.2994	1.355(0 1.3540	1.3528	1.3515	4.3543	4.3560	4.3587		4.3637
0.3468	1.3557	7 1.3546	1.3534	1.3520	4.3704	4.3711	4.3740		4.3779
0.3959	1.356	4 1.3553	1.3541	1.3526	4.3866	4.3876	4.3904		4.3933
0.4498	1.357	1 1.3561	1.3549	1.3533	4.4039	4.4062	4.4091		4.4109
Standard ur ^a Relative s ionic liquid	ncertaint itandard in wate	ies u are $u(T) =$ uncertainties u_r f	0.01 K, $u(n_D) = 5 \times$ for molalities of ionic	$< 10^{-4}$, $u(p) = 0.01$ liquid and amino a	I MPa and the estimates of $u_{\rm r}(m_{\rm IL}) = 0$ cids are $u_{\rm r}(m_{\rm IL}) = 0$	lated uncertainty (K .02 and $u_{\rm t}(m) = 0.0$	k _D) = 0.0029 005, respectively, w	where $m_{\rm IL}$ is the mol	al concentration of

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Table 10 continued

listed in Table 9. It is clear from this table that the values of $\Delta \mu_2^{0*}$ are positive and larger than $\Delta \mu_1^{0*}$ for both the amino acids. This indicates stronger interactions between solute (amino acids) and solvent (aqueous solutions of [BMIM][Ibu]) in the ground state in comparison to the transition state. The magnitude of $\Delta \mu_2^{0*}$ decreases with increase in concentration of [BMIM][Ibu] up to 0.3 mol·kg⁻¹. The higher values of $\Delta \mu_2^{0*}$ for L-alanine suggest that more energy is needed for transfer from ground state solvent to transition state solvent for amino acids with a longer alkyl side [63].

3.5 Refractometric Properties

Experimental refractive index data n_D for glycine in water and in the aqueous solutions of 0.1090, 0.1801 and 0.2642 mol·kg⁻¹ [BMIM][Ibu], along with refractive index values for L-alanine in water and in the aqueous solutions of 0.1110, 0.1800 and 0.2602 mol·kg⁻¹ [BMIM][Ibu], are reported in Table 10. In Figs. S7 and S8 (in supporting information) the refractive index values of glycine and L-alanine in water at T = 298.15, 308.15 and 318.15 K are compared with values reported in Ref. [18]. Refractive index data for glycine and L-alanine in this work are in fairly good agreement with this Ref. [71]. The molar refraction R_D was calculated using Lorentz–Lorenz equation [72]:

$$R_{\rm D} = \left[\frac{n_{\rm D} - 1}{n_{\rm D}^2 + 2}\right] \left(\sum_{i=1}^3 \frac{x_i M_i}{d}\right) \tag{20}$$

where x_i and M_i are the mole fraction and molecular weight of component *i*, respectively, and *d* is solution density. The calculated molar refractions of the investigated solutions are given in Table 10. The molar refractions R_D of ternary (glycine + BMIM][Ibu] + water) solutions with 0.2642 mol·kg⁻¹ BMIM][Ibu], and (L-alanine + [BMIM][Ibu] + water) with 0.2602 mol·kg⁻¹ of BMIM][Ibu] at T = 298.15 K are plotted in Fig. 7.



Fig. 7 The molar refractions R_D of ternary (glycine (*square*) + BMIM][Ibu] + water) solutions with 0.1801 mol·kg⁻¹ BMIM][Ibu]) and (L-alanine (*triangle*) +[BMIM][Ibu] + water) with 0.1800 mol·kg⁻¹ (BMIM][Ibu]) at T = 298.15 K

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The R_D value is directly proportional to molecular polarizability and therefore this quantity is a measure of the ability of molecular orbitals to be shapeless under an electrical field [18]. Furthermore, when the structure of a molecule becomes more complex, its electron cloud becomes more decentralized, and the polarizability of the molecule increases. As it can be seen from this Table, the R_D values increase with increasing concentration of [BMIM][Ibu] in the studied ternary solutions due to its electron cloud becoming more decentralized, which indicates high polarizability of amino acids in the presence of [BMIM][Ibu]. All of these parameters show that the addition of this ionic liquid to the aqueous amino acid solutions has a strong dehydration effect on the investigated solutions.

4 Conclusions

Densities, speeds of sound, viscosities and refractive indices for glycine and L-alanine in water and in the aqueous solutions of 1-butyl-3-methylimidazolium ibuprofenate, [BMI-M][Ibu] have been measured at the experimental temperatures T = 288.15, 298.15, 308.15and 318.15 K. The calculated volumetric and acoustic parameters, such as the partial molar volume of transfer $\Delta_{tr} V_{\phi}^0$ and partial molar isentropic compressibility of transfer $\Delta_{tr} \kappa_{\phi}^0$, indicate dominance of polar-polar and ion-polar interactions between (glycine, L-alanine) and [BMIM][Ibu]. The less negative values of $(\partial^2 V_{\phi}^0 / \partial T^2)_p$ for glycine, and more positive values for L-alanine, in aqueous solutions of [BMIM][Ibu] can be interpreted as an increase in the structure-breaking ability for glycine and decrease of the structure-making power for L-alanine. The reduction in the hydration numbers with increase in temperature and [BMIM][Ibu] concentration expresses the stronger dehydration of glycine and L-alanine at higher concentrations and temperatures. The values of V_{AB} and κ_{AB} characterize the pairwise interaction between amino acids and [BMIM][Ibu]. The more positive values of dB/dT for glycine and less negative values for L-alanine in aqueous [BMIM][Ibu] solutions indicate the promotion of structure-breaking ability in glycine and weakening of the structure-making ability in L-alanine. The greater values of $\Delta \mu_2^{0*}$ for L-alanine than for glycine in aqueous [BMIM][Ibu] solutions show the more effective structure-making ability of L-alanine. High polarizability of amino acids in the presence of [BMIM][Ibu] causes that the molar refractions to have large $R_{\rm D}$ values at high concentration of [BMIM][Ibu]. In general, the dehydration effect of [BMIM][Ibu] on the aqueous solutions of glycine and L-alanine is intensified at high concentration of the ionic liquid.

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