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Densities, Viscosities, Electrical Conductances, and Refractive Indices of Amino Acid + Ionic Liquid ([BMIm]Br) + Water Mixtures at 298.15 K

Hemayat Shekaari* and Fatemeh Jebali

Department of Chemistry, University of Mohaghegh Ardabili, Ardabil, Iran

Densities, viscosities, electrical conductances, and refractive indices of the amino acids glycine, L-alanine, and L-valine in aqueous ionic liquid, 1-butyl-3-methylimidazolium bromide ([BMIm]Br), solutions have been measured at 298.15 K. These data have been used to calculate apparent molar volumes, V_ϕ, viscosity B-coefficients and ion association constants, K_a, for the mixtures studied. The limiting partial molar volumes, V_ϕ^0, and transfer partial molar volumes, $\Delta_{tr}V_\phi^0$, have been determined. It has been observed that both V_ϕ^0 and $\Delta_{tr}V_\phi^0$ values for amino acids increase with increasing ionic liquid concentrations. The linear correlation of V_ϕ^0 and B-coefficient values with the number of carbon atoms in alkyl chain of the amino acids have been used to estimate the contribution of charged end groups (NH_3^+, COO^-). All these parameters was used to interpretate solute−solvent interactions occurring between the various components in these ternary mixtures. Limiting molar conductivities, Λ_0 and ion association constants, K_a of ionic liquid were obtained from the low concentration chemical model (lcCM) of the conductance equation.

Introduction

Amino acids as fundamental structural units of peptides and proteins have an important role in biological systems by affecting solubility, denaturation, and activity of biomolecules.[1−3] The study of the effects of these model compounds in the presence of electrolyte solutions on the thermophysical properties provide important information about solute−solvent and solute−solute interactions on biomolecules.[4,5]

Organic electrolytes can give better insight into the effect of electrostatic and hydrophobic interactions on the stability of amino acids as these compounds are expected to influence macromolecular conformations by weakening attractive or repulsive inter- and intrachain charge−charge interactions and by affecting hydrophobic interactions through the side chains, the alkyl groups. Ionic liquids as organic electrolytes and green solvents containing the bulky cations are known to orient water molecules around their alkyl chain structure-making capability. Ionic liquids undergo hydrophobic hydration in water that is usually understood as the formation of more ordered and rigid structures of water surrounding the solute molecules.[6] Thus, keeping these considerations in mind, in the present work we report densities, d, viscosities, η, molar conductivities, Λ, and refractive indices, n_D, of three amino acids, glycine, L-alanine, and L-valine in solutions of the aqueous ionic liquid, 1-butyl-3-methyl-imidazolium bromide, [BMIm]Br. Apparent molar volumes, V_ϕ, of amino acids were calculated at $T = 298.15$ K and used to calculate the limiting partial molar volumes, V_ϕ^0, and the partial molar volumes of transfer, $\Delta_{tr}V_\phi^0$, of the amino acids from water to the aqueous ionic liquid solutions. The viscosity B-coefficients were calculated by using the Jones−Dole equation.[7] All these parameters were used to interpret solute−solute and solute−solvent interactions occurring between the various components in these ternary mixtures. Molar conductivities of ionic liquid [BMIm]Br in aqueous amino acids solutions have been correlated with the low concentration chemical model (lcCM) of conductance, and ion association constants, K_a, limiting molar conductivity, Λ_0, of ionic liquids have been obtained. The experimental results of refractive indices for these studied mixtures have been reported and fitted by a linear equation.

Experimental Section

Materials. Reagents used in this work, N-methylimidazole (>99 %), 1-bromobutane (>99 %), acetonitrile (GR, >99.8 %), toluene (>99 %), glycine (>99.7 %), L-alanine (>99 %), were obtained from Merck. L-Valine (>99 % in mass fraction) was purchased from Lobachemie (India). Amino acids were dried in vacuum over blue silica gel at room temperature for at least 72 h. The other chemicals were used without further purification. The doubly distilled deionized water was used for the preparation of solutions and had conductance of approximately 0.7 $\mu S \cdot cm^{-1}$.

Synthesis of Ionic Liquid. The ionic liquid, [BMIm]Br, was prepared and purified by using the procedure described in the literature.[8,9] Briefly, [BMIm]Br was synthesized by direct alkylation of N-methylimidazole with an excess of 1-bromobutane in a round-bottom flask at $T = 353$ K for 48 h under a nitrogen atmosphere. The crude product was dissolved in acetonitrile and crystallized by adding dropwise to toluene in an ice bath. The product was dried in high vacuum at $T = 333$ K using a rotary evaporator for at least 4 h in 0.7 kPa. The synthesized [BMIm]Br has purity greater than mass fraction 0.99. The trace amount of water in ionic liquid was removed in high vacuum for at least 48 h. Water content found by Karl Fischer method in the [BMIm]Br was less than mass fraction 0.02. This synthesized ionic liquid was analyzed by ^{1}H NMR (Bruker Av-300) and FTIR (Perkin-Elmer, Spectrum RXI) to confirm the absence of any major impurities, and they were found to be in good agreement with those reported in the literature.[10,11]

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* Corresponding author. Telephone: +98-451-5514702. Fax: +98-451-5514701. E-mail: hemayat@yahoo.com (H.S.).

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Apparatus and Procedure. The solutions containing ionic liquid and amino acids were prepared by filling glass vials and closing them tightly. The sample was taken from the vial with a syringe and immediately injected into the apparatus. The mass of chemicals was determined using a Sartrious analytical balance AG TE214S with an uncertainty $\pm 1 \cdot 10^{-7}$ kg.

The densities of solutions were measured using a vibrating-tube densimeter DMA 4500 M (Anton Paar, Austria). The apparatus was calibrated with doubly distilled, deionized, and degassed water and dry air at atmospheric pressure. Density is extremely sensitive to temperature, so it was kept constant within $\pm 1.0 \cdot 10^{-3}$ K using the built-in Peltier technique. The apparatus was also tested with the density of a known molality of aqueous NaCl using the data given by Pitzer et al.[12] The uncertainties of density measurements was better than $\pm 1.0 \cdot 10^{-5}$ $g \cdot cm^{-3}$. Triplicate measurements were done to obtain the as the average value of density.

The viscosities were measured using an Ubbelohde-type viscometer, which has a flow time of about 200 s for water at 298.15 K. The viscometer was calibrated with doubly distilled deionized water. Viscosity of solution, η, is given by the following equation

$$\frac{\eta}{d} = Lt - \frac{K}{t} \tag{1}$$

where d is the density, t is the flow time of the solution and L and K are the viscometer constants. A digital stopwatch with a resolution of 0.01 s has been used for the measurement of flow time measurement. The estimated uncertainly of the experimental viscosity was $\pm$ 0.02 mPa·s.

Conductance measurements were carried out on a digital conductivity meter (Metrohm model 712) with a sensitivity of 0.1 %. The cell constant was calibrated with aqueous KC1 solution. About 50 mL of doubly distilled deionized water and different mass of amino acid was placed in the conductivity cell and the cell was closed. Pure ionic liquid was weighed and added with a syringe to the cell contains the solvent. Circulating water from a thermostatically regulated bath around the sample holder with double wall was done to maintain the temperature with a precision of 0.03 K. The conductivity cell was purged with nitrogen during each run.

Refractive indices of the studied mixtures were determined using a digital refractometer (ATAGO-DRA1, Japan) with an uncertainty of $\pm 1 \cdot 10^{-4}$. 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 is working properly. Calibration was checked with pure liquids of known refractive index. The temperature was controlled using a circulating bath thermostat (Julabo NP, Germany) with a stability of ± 0.01 K.

Results and Discussion

Volumetric Properties. The experimental densities, d, of amino acid + [BMIm]Br + water mixtures as a function of amino acid concentration, m (glycine, L-alanine and L-valine), are reported in Table 1. The apparent molar volumes, V_ϕ, of amino acid in aqueous [BMIm]Br solutions were calculated from the densities of the solutions using the following equation:[13]

$$V_\phi = \frac{M}{d} - \frac{(d - d_0)}{mdd_0} \tag{2}$$

where M is the molar mass of the amino acid, m is the molality of the amino acid in [BMIm]Br + water mixture, d and d_0 are the densities of (amino acid + [BMIm]Br + water) ternary mixtures and reference solvent (desired molality of aqueous [BMIm]Br), respectively.

The values of V_ϕ for glycine, L-alanine, L-valine in aqueous 0.1 $mol \cdot kg^{-1}$ [BMIm]Br solutions have been compared (Figure of 1 of the Supporting Information), which have the order: glycine < L-alanine < L-valine. The results in Table 1 show that the V_ϕ values increase with increasing size of the alkyl group of the amino acids and with increasing the concentration of [BMIm]Br. In the cases where the molality dependence of V_ϕ was found to be either negligible or having no definite trend, the value of the limiting partial molar volume V_ϕ^0 was evaluated by taking an average of all the data points. In all other cases, the value of the V_ϕ^0 value was obtained by least-squares fitting to the following equation[14]

$$V_\phi = V_\phi^0 + S_\nu \cdot m \tag{3}$$

where S_ν is the experimental slope which is also considered as volumetric virial pairwise interaction coefficient. The sign of S_ν shows that the nature of the solute–solute interactions, while V_ϕ^0 values reflect the presence of solute–solvent interactions.[15,16] The values of V_ϕ^0 and S_ν are given in Table 2. The positive values of S_ν for mixtures containing glycine, and L-alanine suggest that the pairwise interaction is dominated by the interaction of the charged functional groups with ions of ionic liquid. The variation in the values of S_ν with side-chain position of amino acids indicates that the methyl group modulates the interaction of the charged end-groups in the pairwise interaction. As shown in Table 2, the positive values of S_ν suggest that zwitterionic end group of amino acids with ionic liquid has a strong dehydrations effect on the amino acids. The values of V_ϕ^0 are positive for all the amino acids studied at all the molalities of aqueous [BMIm]Br solutions. The order of V_ϕ^0 values is: glycine < L-alanine < L-valine. This order shows that, in general, V_ϕ^0 values increase with the increasing molar mass of amino acid, as also reported in literature.[17] This table also shows that the V_ϕ^0 values of amino acids increase with an increase in the concentration of aqueous [BMIm]Br. These results are similar to the values of V_ϕ^0 obtained from studied amino acids in aqueous tetraethylammonium bromide solutions at all molalities.[1] The possible reasons for this behavior could be due to weaker hydrophobic interactions in amino acids.[18] Similar linear correlations have been observed earlier for homologous series of amino acids in aqueous electrolyte solutions.[19]

At each molality, the V_ϕ^0 values indicate linear variation with the number of carbon atoms in alkyl chain of amino acids. This linear variation is represented by[20]

$$V_\phi^0 = V_\phi^0(\mathrm{NH_3}^+, \mathrm{COO}^-) + n_c V_\phi^0(\mathrm{CH_2}) \tag{4}$$

where n_c is the number of carbon atoms in the alkyl chain of the amino acids; V_ϕ^0 (NH_3^+, COO^-) and V_ϕ^0 (CH_2) are the zwitterionic end groups and the methylene group contribution to V_ϕ^0, respectively. The values of V_ϕ^0 (NH_3^+, COO^-) and V_ϕ^0 (CH_2), calculated by a least-squares regression analysis have been calculated (Table 1 of the Supporting Information). Since the alkyl chains of the homologous series of the amino acids studied in this work are CH_2-(glycine), CH_3CH-(L-alanine), CH_3CH_3CHCH-(L-valine), the values of V_ϕ^0 (CH_2) obtained by this procedure characterizes the mean contribution of the CH- and CH_3 groups to V_ϕ^0 of the amino acids. The contributions of the other alkyl chains of the amino acids reported in this table were calculated as follows:[21]

Table 1. Densities, d, and Apparent Molar Volumes, V_ϕ, of Amino Acids in Aqueous [BMIm]Br Solutions as a Function of Amino Acids Concentration, m at 298.15 K

m	10^3d	10^6V_ϕ	m	10^3d	10^6V_ϕ	m	10^3d	10^6V_ϕ	m	10^3d	10^6V_ϕ	m	10^3d	10^6V_ϕ
$mol \cdot kg^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$	$mol \cdot kg^{-1}$	$kg \cdot m^{-3}$	$m^3 \cdot mol^{-1}$
Glycine														
$^a m_{IL} = 0.0000\ mol \cdot kg^{-1}$			$m_{IL} = 0.0915\ mol \cdot kg^{-1}$			$m_{IL} = 0.1850\ mol \cdot kg^{-1}$			$m_{IL} = 0.2866\ mol \cdot kg^{-1}$			$m_{IL} = 0.3496\ mol \cdot kg^{-1}$		
0.0000	0.99704[28]		0.0000	1.00177		0.0000	1.00646		0.0000	1.01129		0.0000	1.01439	
0.0521	0.99870	43.19	0.0978	1.00485	43.41	0.0952	1.00944	43.56	0.1024	1.01448	43.62	0.1062	1.01770	43.57
0.0997	1.00021	43.17	0.1375	1.00609	43.43	0.1336	1.01063	43.58	0.1348	1.01548	43.64	0.1314	1.01848	43.59
0.1577	1.00202	43.30	0.1924	1.00780	43.44	0.2048	1.01283	43.60	0.2058	1.01766	43.68	0.1926	1.02035	43.67
0.1992	1.00332	43.30	0.2546	1.00971	43.51	0.2812	1.01516	43.66	0.2552	1.01917	43.69	0.2466	1.02199	43.73
0.2235	1.00407	43.34	0.2975	1.01102	43.54	0.2881	1.01537	43.66	0.2824	1.01999	43.72	0.2900	1.02330	43.75
0.2902	1.00611	43.46	0.3472	1.01253	43.59	0.3471	1.01716	43.69	0.3505	1.02205	43.74	0.3437	1.02490	43.83
0.3266	1.00722	43.49	0.4056	1.01429	43.63	0.4022	1.01882	43.71	0.3955	1.02340	43.77	0.3981	1.02652	43.86
0.4495	1.01093	43.60	0.4394	1.01531	43.64	0.4644	1.02067	43.76	0.4375	1.02465	43.79	0.4367	1.02765	43.92
0.5179	1.01294	43.71												
L-Alanine														
$m_{IL} = 0.0000\ mol \cdot kg^{-1}$			$m_{IL} = 0.0970\ mol \cdot kg^{-1}$			$m_{IL} = 0.1833\ mol \cdot kg^{-1}$			$m_{IL} = 0.2863\ mol \cdot kg^{-1}$			$m_{IL} = 0.3651\ mol \cdot kg^{-1}$		
0.0000	0.99704		0.0000	1.00197		0.0000	1.00634		0.0000	1.01140		0.0000	1.01507	
0.0499	0.99855	58.83	0.0551	1.00361	59.18	0.0560	1.00799	59.36	0.0531	1.01292	60.01	0.0617	1.01705	60.77
0.0849	0.99960	58.87	0.1058	1.00510	59.27	0.1016	1.00930	59.58	0.108	1.01447	60.13	0.1058	1.01826	60.80
0.1397	1.00123	58.93	0.1495	1.00636	59.41	0.1453	1.01055	59.67	0.1514	1.01568	60.19	0.1501	1.01947	60.81
0.1784	1.00237	58.98	0.1928	1.00759	59.55	0.1956	1.01196	59.82	0.2026	1.01709	60.30	0.1982	1.02077	60.85
0.2346	1.00402	59.01	0.2493	1.00918	59.69	0.2459	1.01334	60.00	0.2483	1.01833	60.39	0.2445	1.02201	60.89
0.2731	1.00513	59.08	0.2907	1.01031	59.84	0.2983	1.01477	60.12	0.2879	1.01940	60.44	0.2961	1.02338	60.93
0.3275	1.00670	59.11	0.3454	1.01180	59.98	0.3419	1.01595	60.21	0.344	1.02089	60.55	0.3381	1.02449	60.95
0.3551	1.00746	59.22	0.3882	1.01294	60.11	0.394	1.01732	60.36	0.3983	1.02231	60.66	0.4006	1.02612	61.00
0.4168	1.00923	59.21	0.4541	1.01470	60.23	0.4529	1.01886	60.48	0.4539	1.02375	60.75	0.4586	1.02762	61.04
0.4513	1.01016	59.33												
L-Valine														
$m_{IL} = 0.0000\ mol \cdot kg^{-1}$			$m_{IL} = 0.0909\ mol \cdot kg^{-1}$			$m_{IL} = 0.1797\ mol \cdot kg^{-1}$			$m_{IL} = 0.2670\ mol \cdot kg^{-1}$			$m_{IL} = 0.3564\ mol \cdot kg^{-1}$		
0.0000	0.99704		0.0000	1.00154		0.0000	1.00597		0.0000	1.01020		0.0000	1.01319	
0.1173	1.00017	90.37	0.0505	1.00287	90.57	0.0489	1.00712	89.79	0.0566	1.01149	93.50	0.0535	1.01532	97.94
0.1402	1.00077	90.39	0.1029	1.00423	90.66	0.1040	1.00846	89.92	0.105	1.01265	92.87	0.1052	1.01654	95.15
0.1894	1.00203	90.54	0.1488	1.00540	90.76	0.1476	1.00955	90.04	0.1517	1.01379	92.45	0.151	1.01773	93.49
0.2512	1.00359	90.67	0.1975	1.00662	90.86	0.1989	1.01084	90.15	0.1994	1.01498	92.04	0.2007	1.01897	92.74
0.2973	1.00474	90.74	0.2489	1.00789	90.95	0.2421	1.01192	90.25	0.2511	1.01626	91.77	0.2519	1.02023	92.30
0.3211	1.00532	90.81	0.3025	1.00920	91.02	0.2892	1.01314	90.41	0.3008	1.01748	91.59	0.2948	1.02130	91.98
0.3841	1.00684	90.94	0.3557	1.01047	91.13	0.3436	1.01452	90.46	0.3385	1.01839	91.52	0.3431	1.02251	91.67
0.4378	1.00811	91.05	0.3928	1.01134	91.21	0.3870	1.01558	90.59	0.387	1.01954	91.47	0.3948	1.02378	91.45
			0.4316	1.01225	91.25	0.4515	1.01716		0.4376	1.02073	91.43	0.4346	1.02466	91.53

[a] m_{IL} is the molality of ionic liquid.

Table 2. Limiting Partial Molar Volumes for Amino Acids in Aqueous [BMIm]Br Solutions at 298.15 K

system	m_{IL} $mol \cdot kg^{-1}$	$10^6V\phi^0$ $m^3 \cdot mol^{-1}$	10^6S_ν $m^3 \cdot mol^{-2} \cdot kg$	R^2	$\sigma(V_\phi)$
glycine + water	0.0000	43.09 ± 0.01, 43.2[29]	1.16 ± 0.06	0.9805	0.02
[BMIm]Br + Gly + water	0.0915	43.33 ± 0.01	0.73 ± 0.04	0.9853	0.01
[BMIm]Br + Gly + water	0.1850	43.51 ± 0.01	0.53 ± 0.02	0.9845	0.01
[BMIm]Br + Gly + water	0.2866	43.46 ± 0.01	0.50 ± 0.02	0.9873	0.01
[BMIm]Br + Gly + water	0.3496	43.58 ± 0.01	1.05 ± 0.03	0.9949	0.01
L-Alanine + water	0.0000	58.77 ± 0.02, 60.5[30]	1.17 ± 0.07	0.9726	0.03
[BMIm]Br + L-Ala + water	0.0970	59.01 ± 0.01	2.78 ± 0.03	0.9958	0.03
[BMIm]Br + L-Ala + water	0.1833	59.27 ± 0.02	2.77 ± 0.09	0.9913	0.04
[BMIm]Br + L-Ala + water	0.2863	59.93 ± 0.01	1.82 ± 0.01	0.9993	0.01
[BMIm]Br + L-Ala + water	0.3651	60.72 ± 0.01	0.69 ± 0.02	0.9935	0.01
L-Valine + water	0.0000	90.12 ± 0.01, 91.0[31]	2.14 ± 0.05	0.9967	0.02
[BMIm]Br + L-Val + water	0.0909	90.49 ± 0.01	1.79 ± 0.03	0.9976	0.01
[BMIm]Br + L-Val + water	0.1797	93.05 ± 0.10	−5.32 ± 0.50	0.9293	0.21
[BMIm]Br + L-Val + water	0.2670	93.36 ± 0.01	−5.22 ± 0.02	0.8685	0.28
[BMIm]Br + L-Val + water	0.3564	96.71 ± 0.82	−14.42 ± 2.96	0.7719	1.09

$$V_\phi^0(CH_3) = 1.5V_\phi^0(CH_2) \tag{5}$$

$$V_\phi^0(CH) = 0.5V_\phi^0(CH_2) \tag{6}$$

Larger values of V_ϕ^0 (NH_3^+, COO^-) than V_ϕ^0 (CH_2) at high concentrations of ionic liquid indicate that the interactions of the ions of [BMIm]Br with the zwitterionic groups of the amino acids dominate compared to those of the hydrophobic group [BMIm]Br interactions. In addition, the difference in the molar masses of (NH_3^+, COO^-) and CH_2 groups also accounts for the larger V_ϕ^0 values of the former.

Table 3. Viscosities, η, of Some Amino Acids in Aqueous [BMIm]Br at 298.15 K

$\frac{c}{\text{mol}\cdot\text{m}^{-3}}$	$\frac{10^3\,\eta}{\text{Pa}\cdot\text{s}}$	$\frac{c}{\text{mol}\cdot\text{m}^{-3}}$	$\frac{10^3\,\eta}{\text{Pa}\cdot\text{s}}$	$\frac{c}{\text{mol}\cdot\text{m}^{-3}}$	$\frac{10^3\,\eta}{\text{Pa}\cdot\text{s}}$	$\frac{c}{\text{mol}\cdot\text{m}^{-3}}$	$\frac{10^3\,\eta}{\text{Pa}\cdot\text{s}}$	$\frac{c}{\text{mol}\cdot\text{m}^{-3}}$	$\frac{10^3\,\eta}{\text{Pa}\cdot\text{s}}$
				Glycine					
${}^a m_{IL} = 0.0000$ mol·kg^{-1}		$m_{IL} = 0.0915$ mol·kg^{-1}		$m_{IL} = 0.1850$ mol·kg^{-1}		$m_{IL} = 0.2866$ mol·kg^{-1}		$m_{IL} = 0.3496$ mol·kg^{-1}	
0.0520	0.881	0.0983	0.968	0.0961	0.994	0.1039	1.016	0.1081	1.040
0.0997	0.892	0.1383	0.974	0.1350	1.004	0.1369	1.024	0.1338	1.046
0.1580	0.910	0.1939	0.984	0.2074	1.023	0.2094	1.045	0.1965	1.056
0.1999	0.920	0.2571	0.990	0.2855	1.038	0.2601	1.060	0.2520	1.075
0.2244	0.929	0.3008	0.995	0.2925	1.042	0.2880	1.069	0.2968	1.089
0.2920	0.939	0.3515	1.001	0.3530	1.061	0.3582	1.092	0.3522	1.109
0.3289	0.945	0.4114	1.007	0.4098	1.080	0.4047	1.107	0.4086	1.128
0.4544	0.965	0.4461	1.013	0.4740	1.096	0.4483	1.117	0.4488	1.151
0.5246	0.980								
				L-Alanine					
$m_{IL} = 0.0000$ mol·kg^{-1}		$m_{IL} = 0.0970$ mol·kg^{-1}		$m_{IL} = 0.1833$ mol·kg^{-1}		$m_{IL} = 0.2863$ mol·kg^{-1}		$m_{IL} = 0.3651$ mol·kg^{-1}	
0.0532	0.886	0.0553	0.950	0.0564	0.992	0.0538	1.044	0.0628	1.088
0.0910	0.891	0.1063	0.964	0.1025	1.006	0.1096	1.059	0.1077	1.102
0.1498	0.897	0.1504	0.978	0.1468	1.021	0.1538	1.068	0.1530	1.112
0.1918	0.902	0.1943	0.991	0.1979	1.039	0.2061	1.083	0.2023	1.126
0.2526	0.912	0.2516	1.011	0.2492	1.054	0.2528	1.093	0.2499	1.140
0.2941	0.921	0.2937	1.024	0.3027	1.072	0.2935	1.103	0.3030	1.159
0.3537	0.928	0.3495	1.039	0.3473	1.090	0.3512	1.122	0.3464	1.173
0.3827	0.936	0.4608	1.073	0.4008	1.105	0.4072	1.136	0.4110	1.197
0.4512	0.951			0.4614	1.129	0.4647	1.147	0.4712	1.212
0.4876	0.957								
				L-Valine					
${}^a m_{IL} = 0.0000$ mol·kg^{-1}		$m_{IL} = 0.0909$ mol·kg^{-1}		$m_{IL} = 0.1797$ mol·kg^{-1}		$m_{IL} = 0.2670$ mol·kg^{-1}		$m_{IL} = 0.3564$ mol·kg^{-1}	
0.1173	0.892	0.0506	0.936	0.0492	0.975	0.0572	1.025	0.0543	1.051
0.1403	0.899	0.1033	0.959	0.1049	0.998	0.1063	1.040	0.1069	1.070
0.1898	0.906	0.1496	0.986	0.1490	1.012	0.1538	1.058	0.1537	1.089
0.2521	0.916	0.1988	1.007	0.2011	1.038	0.2024	1.081	0.2045	1.116
0.2987	0.938	0.2509	1.030	0.2450	1.061	0.2552	1.112	0.2570	1.138
0.3228	0.943	0.3053	1.057	0.2930	1.083	0.3060	1.131	0.3011	1.156
0.3867	0.958	0.3594	1.076	0.3486	1.111	0.3447	1.150	0.3508	1.188
0.4413	0.979	0.3972	1.090	0.3930	1.133	0.3945	1.177	0.4042	1.224
		0.4369	1.104	0.4592	1.165	0.4466	1.195	0.4453	1.239

[a] m_{IL} and c are the molality of ionic liquid, and molar concentration of amino acid, respectively.

Limiting thermodynamic properties of transfer yield qualitative and quantitative information regarding the interactions of a cosolvent and a solute without having to take into account the effects of solute−solute interactions as at infinite dilution the interactions between solute molecules are negligible. The limiting partial molar volumes of transfer, $\Delta_{tr}V_\phi^0$, for the amino acids from water to [BMIm]Br solutions were calculated as follows:

$$\Delta_{tr}V_\phi^0 = V_\phi^0([\text{BMIm}]\text{Br} + \text{water}) - V_\phi^0(\text{water}) \qquad (7)$$

The $\Delta_{tr}V_\phi^0$ values have positive values for glycine, L-alanine, and L-valine (Table 2 of the Supporting Information). The values of $\Delta_{tr}V_\phi^0$ for these amino acids increase positively with increasing concentration of [BMIm]Br. The uncertainties in the values of volume of transfer are calculated as the root mean squares of the uncertainties associated with the apparent molar properties at infinite dilution.

An increase in the concentration of cosolute [BMIm]Br, results in a positive $\Delta_{tr}V_\phi^0$ indicating an enhancement in the ion−ion interaction between the zwitterionic centers of the amino acids and the ion of the ionic liquid.

Viscosity B-Coefficients. The measured viscosities, η, for (amino acid + [BMIm]Br + water) mixtures at $T = 298.15$ K are tabulated in Table 3. The results show an increase in viscosity of solutions studied with an increase in concentration of ionic liquid, [BMIm]Br. This is due to the fact that with the increasing of ionic liquid concentration, the number of collision between the molecules also increases to result in a loss of kinetic energy, therefore, the molecules tend to stack together to induce the increase in the viscosity. The values of η, for glycine, L-alanine, L-valine in aqueous 0.2 mol·kg^{-1} [BMIm]Br solutions have been compared in Figure 1, which have the order: glycine < L-alanine < L-valine. This is possible due to stronger hydrophobic−hydrophobic interactions at longer alkyl chain of amino acids. Most studies on viscosity are confined to the description of dilute solutions of solutes via determination of the *A*- and *B*-coefficients in the Jones−Dole equation[22]

$$\frac{\eta}{\eta_0} = 1 + Ac^{1/2} + Bc \qquad (8)$$

where η and η_0 are the viscosities of (amino acid + [BMIm]Br + water) ternary mixtures and reference solvent ([BMIm]Br + water), respectively, and c is the molar concentration of amino acid in the (amino acid + [BMIm]Br + water) ternary mixtures. The *A*-coefficient, whose value generally is positive, is a measure of solute−solute interactions and the *B*-coefficient is an empirical constant which depends on solute−solvent interactions and can have positive or negative, values. The values of *A* and *B*

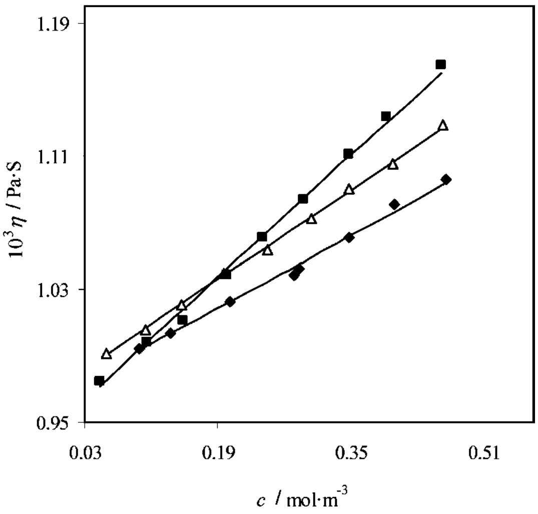

Figure 1. Comparison of viscosities, η of amino acids in 0.2 mol·kg^{-1} aqueous [BMIm]Br solutions: ◆, glycine; Δ, L-alanine; ■, L-valine at 298.15 K.

were calculated by the method of least-squares by fitting the experimental viscosity data in the Jones−Dole equation (Table 3 of the Supporting Information). The viscosity *B*-coefficients increase with increase in molar mass and size of alkyl side chain of amino acids and are large as compared to *A* values, supporting the behavior of V_ϕ^0, S_ν, respectively. This again suggests the dominance of solute−solvent interactions over solute−solute interactions. The values of viscosity *B*-coefficients in inorganic salts solutions are large as compared with those in organic salts that indicate increasing interactions between amino acid and inorganic salts.[23] The viscosity *B*-coefficients given in this table reflect the net structural effects of charged end groups (NH_3^+,COO^-)and the hydrophobic CH_2 groups on the amino acids.[24] These two effects can be separated by noting that the *B*-coefficients are linear in n_c, that is

$$B = B(\mathrm{NH_3}^+, \mathrm{COO}^-) + n_c B(\mathrm{CH_2}) \tag{9}$$

The regression parameters, $B(NH_3^+,COO^-)$, the zwitterionic group contribution, and $B(CH_2)$, the methylene group contribution to the viscosity *B*-coefficient, have been calculated (Table 4 of the Supporting Information). It can be seen from this table that values of $B(NH_3^+,COO^-)$ increase while $B(CH_2)$ values decrease with increasing concentration of ionic liquid in solutions, indicating that the zwitterionic groups break while CH_2 groups enhance the structures of aqueous ionic liquid solutions. Moreover, it is observed that *B*-coefficients show a linear correlation with the limiting partial molar volumes, V_ϕ^0, for amino acids in aqueous [BMIm]Br solutions. The coefficients A_1 and A_2 of the equation

$$B = A_1 + A_2 V_\phi^0 \tag{10}$$

have been calculated (Table 5 of the Supporting Information). Similar correlations for amino acids in electrolytes were observed.[22] This is due to the partial molar volumes and *B*-coefficients reflect the solute−solvent interactions in solutions.

Limiting Molar Conductivities. The calculated molar conductivities, Λ, using the measured specific conductivities in the aqueous solutions of the ionic liquid at different concentration of amino acids are given in Table 4. The values of Λ for glycine, L-alanine, L-valine in aqueous 0.4 mol·kg^{-1} [BMIm]Br solutions have been compared in Figure 2. It is shown that the molar conductivities, Λ, decrease with increasing ionic liquid concentration. An increase in the ionic liquid concentration causes the formation of ion pairs in the dilute region and stronger ion association in the studied mixtures and then a decreasing molar conductivity. Increasing amino acids lead to formation−hydration causing decreasing ions as the limiting molar conductivity decreases.

There are many different equations for the treatment of conductance data.[25] The low concentration chemical model (lcCM) is recently applied widely for the correlation of conductance data in aqueous and nonaqueous electrolyte solutions.[26] Analysis of conductivity data in the framework of the low-concentration chemical model (lcCM) uses the following set of equations:

$$\Lambda = \alpha[\Lambda_0 - S(c\alpha)^{1/2} + Ec\alpha \ln(c\alpha) + J_1 c\alpha + J_2(c\alpha)^{3/2}] \tag{11}$$

where ion association constant, K_a is defined as

$$K_a = \frac{1 - \alpha}{\alpha^2 c \gamma_\pm^2} \tag{12}$$

where

$$\ln \gamma_\pm = -\frac{\kappa q}{1 + \kappa R} \tag{13}$$

$$\kappa^2 = \frac{16000 N_A z^2 e^2 \alpha c}{\varepsilon_0 \varepsilon k_B T} \tag{14}$$

$$q = \frac{z^2 e^2}{8\pi \varepsilon_0 \varepsilon k_B T} \tag{15}$$

and Λ and Λ_0 are the molar conductivities and limiting molar conductivity, respectively; α is the fraction of oppositely charged ions acting as ion pairs; *R* is a distance parameter; and $\gamma_\pm$ is the corresponding mean activity coefficient of the free ions. The coefficients *E*, J_1, and J_2 required for calculations were taken from ref 26. The rest of the parameters have the usual meanings. Three-parameter fits of the molar conductivity data yield the ion-association constant, K_a, the limiting molar conductivity, Λ_0, and distance parameter, *R*, by nonlinear least-squares iteration. K_a, Λ_0, and *R* parameters are calculated (Table 6 of the Supporting Information).

As can be shown from this table, the ion association constants decrease with increasing concentration of amino acids. Increasing concentration of amino acids leads to the formation of ion pairs that solute−solvent interactions decrease and Λ_0 and K_a values decrease. Λ_0 values in aqueous [BMIm]Br solutions of amino acids are in agreement with values obtained for tetraalkylammonium bromide solutions.[27] This result supports the conclusion obtained by considering volumetric results.

Refractive Index Data Correlation. Experimental refractive index data, n_D for glycine, L-alanine, and L-valine in aqueous solutions of [BMIm]Br were measured as a function of the molality of the amino acids (Table 7 of the Supporting Information). The results indicate the n_D values increase as the concentration of amino acid increases. The values of the refractive indices of the investigated ternary mixtures have been fitted with the following equation:

$$n_D = n_D^* + Am \tag{16}$$

where *m* is the molality of the amino acid, at a fixed concentration of aqueous ionic liquid solution, n_D* is the refractive index of solvent ([BMIm]Br + water) and *A* is an experimental parameter (Table 8 of the Supporting Information).

Table 4. Molar Conductivities, Λ, of Aqueous Solutions of [BMIm]Br as a Function of Molar Concentrations, *c*, in Amino Acids at 298.15 K

c / mol·m^{-3}	$10^4\ \Lambda$ / S·m^2·mol^{-1}	c / mol·m^{-3}	$10^4\ \Lambda$ / S·m^2·mol^{-1}	c / mol·m^{-3}	$10^4\ \Lambda$ / S·m^2·mol^{-1}	c / mol·m^{-3}	$10^4\ \Lambda$ / S·m^2·mol^{-1}
Gly (0.0000 mol·kg^{-1})		Gly (0.4399 mol·kg^{-1})		Gly (0.9167 mol·kg^{-1})		Gly (1.5605 mol·kg^{-1})	
0.7166	153.45	0.7536	148.05	0.5618	143.04	2.2841	136.30
1.4858	148.11	1.6232	146.55	1.2704	139.92	3.3609	133.61
2.2747	146.33	2.4734	145.17	2.0875	138.95	4.5421	131.81
3.8920	145.01	3.3237	144.26	2.9430	138.18	5.7299	130.41
5.6605	142.17	4.9920	141.36	4.7496	134.68	8.1968	127.18
7.3830	139.40	6.5250	139.33	7.4819	131.47	10.5787	124.25
9.0397	137.41	9.9324	134.47	9.9461	129.06	13.0717	121.82
11.6037	134.63	13.4493	130.61	12.3656	126.86	16.8046	118.39
14.3123	131.86	15.6394	128.11	15.5256	124.41	20.6811	115.05
17.4745	128.88	19.4204	124.74	19.7007	121.20	25.8041	111.36
21.0378	125.73	23.1757	121.92	23.4225	118.59	32.2518	107.20
24.7457	122.78	28.0324	118.45	27.5082	115.91	38.6931	103.52
L-Ala (0.0000 mol·kg^{-1})		L-Ala (0.4058 mol·kg^{-1})		L-Ala (0.8515 mol·kg^{-1})			
0.7166	153.45	0.6314	111.53	0.6559	103.14		
1.4858	148.11	1.1691	110.29	1.4300	100.77		
2.2747	146.33	1.8943	109.25	2.0336	99.28		
3.8920	145.01	2.6320	108.22	4.2180	90.80		
5.6605	142.17	5.5766	106.08	7.0847	81.94		
7.3830	139.40	8.6212	104.10	10.0563	74.53		
9.0397	137.41	11.7720	101.52	13.7626	66.21		
11.6037	134.63	15.2168	99.17	16.5637	59.96		
14.3123	131.86	19.3491	96.39	19.9945	52.67		
17.4745	128.88	23.0502	94.14	23.4121	47.67		
21.0378	125.73	26.8763	91.83				
24.7457	122.78	30.7773	89.81				
L-Val (0.0000 mol·kg^{-1})		L-Val (0.4410 mol·kg^{-1})		L-Val (1.6986 mol·kg^{-1})			
0.7166	153.45	0.2912	128.26	0.7075	115.47		
1.4858	148.11	0.7218	124.41	1.2993	113.49		
2.2747	146.33	1.2980	119.37	1.9455	111.72		
3.8920	145.01	2.22243	117.42	2.6938	110.35		
5.6605	142.17	3.9826	107.53	4.2447	106.52		
7.3830	139.40	5.9328	102.79	5.5032	104.84		
9.0397	137.41	8.3832	97.86	7.4283	101.75		
11.6037	134.63	11.2958	95.07	9.4078	98.98		
14.3123	131.86	13.2269	91.97	13.1152	94.216		
17.4745	128.88	15.5316		16.2240	90.65		

This table shows that n_D vs concentration are found to increase linearly with increasing amount of amino acids in aqueous [BMIm]Br of amino acid. The values of n_D for glycine, L-alanine, L-valine in aqueous 0.2 mol·kg^{-1} [BMIm]Br solutions have been compared (Figure of 2 of the Supporting Information). As can be seen the n_D value increase with increasing side-chain length of amino acid.

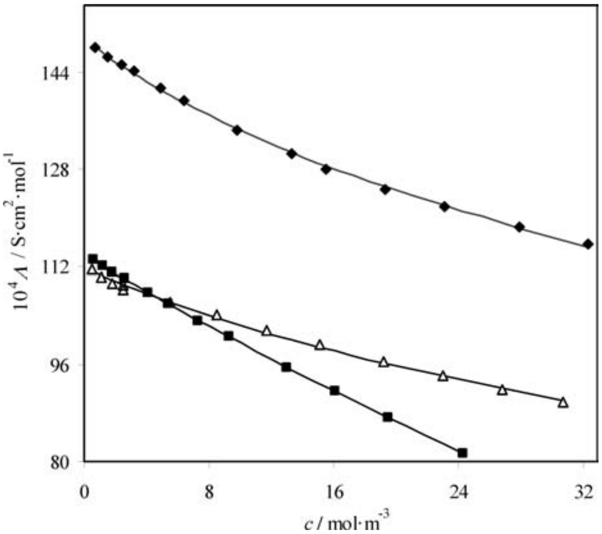

Figure 2. Comparison of molar conductivity, Λ of [BMIm]Br in 0.4 mol·kg^{-1} aqueous solutions; ◆, glycine; ▲, L-alanine; □, L-valine at 298.15 K.

Conclusions

Density, viscosity, electrical conductance and refractive index data of three amino acids, glycine, L-alanine, and L-valine in aqueous ionic liquid, 1-butyl-3-methylimidazolium bromide ([BMIm]Br) solutions have been measured at T = 298.15 K. Apparent molar volume, V_ϕ, limiting partial molar volume, V_ϕ^0 and transfer partial molar volume, $\Delta_{tr}V_\phi^0$, and side-chain contribution V_ϕ^0(R) of the amino acids, have been computed. Values of V_ϕ^0 (NH_3^+, COO^-) larger than those of V_ϕ^0 (CH_2) indicate that the interactions of the ions of [BMIm]Br with the zwitterionic groups of the amino acids dominate compared to those of the hydrophobic group [BMIm]Br interactions. The values of $\Delta_{tr}V_\phi^0$ have positive values for these amino acids. The viscosity *A*- and *B*-coefficients were calculated by using Jones−Dole equation. The results show that the values of B (NH_3^+,COO^-) increase, while $B(CH_2)$ values decrease with increasing concentration of ionic liquid solutions, indicating that the zwitterionic groups break while CH_2 groups enhance the structures of aqueous ionic liquid solutions. The conductometric studies show that the values of Λ_0 and K_a of this ionic liquid in amino acids solutions decrease with increasing amino acid content in solutions. This is due to increasing medium viscosity with increasing amino acid concentration and attraction between ionic liquid and amino acid and, hence, presolvation of ions by amino acid molecules, causing an increase of hydrodynamic radii of ions and a decrease of their mobility.

Supporting Information Available:

Contributions of zwitterionic group (NH_3^+, COO−), CH_2 group and other alkyl chains to the infinite dilution apparent molar volume, transfer partial molar volumes. The values of *A*- and *B*-parameters of the Jones−Dole equation, viscosity *B*-coefficients of zwitterionic (NH_3^+, COO−) and CH_2 *g*roups, the coefficients A_1 and A_2 of eq 10, ion association constants, limiting molar conductivity, distance parameters, refractive indices, parameters of eq 16, of (amino acid + [BMIm]Br + water). This material is available free of charge via the Internet at http://pubs.acs.org.

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