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Densities and Speeds of Sound of Glycine, L-Alanine, and L-Valine in Aqueous 1-Ethyl-3-methylimidazolium Chloride Solutions at Different Temperatures

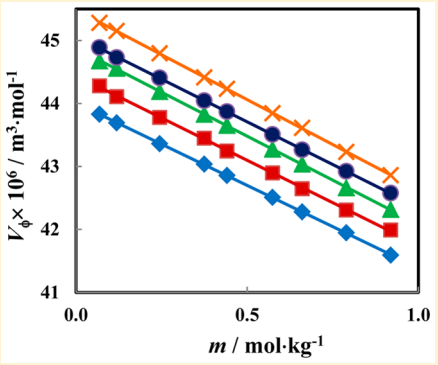
Amalendu Pal,*[,‡] Harsh Kumar,[§] Ritu Maan,[†] and Harish Kumar Sharma[†]

[‡]Department of Chemistry, Kurukshetra University, Kurukshetra 136119, Haryana, India

[§]Department of Chemistry, Dr. B.R. Ambedkar National Institute of Technology, Jalandhar 144011, Punjab, India

[†]Department of Chemistry, M. M. University, Mullana, Ambala, Haryana, India

ABSTRACT: The interactions of amino acids + water + 1-ethyl-3-methylimidazolium chloride [emim][Cl] solutions have been studied at different temperatures using volumetric and acoustic measurements. The density (ρ) and speed of sound (u) of glycine/L-alanine/L-valine + water + 1-ethyl-3-methylimidazolium chloride solutions have been measured at temperatures T = (288.15, 293.15, 298.15, 303.15, and 308.15) K and experimental pressure of 0.1 MPa. The apparent molar properties, standard partial molar properties, and partial molar properties of transfer have been determined from experimentally measured densities and speeds of sound. The resulting values of V_ϕ^0, ΔV_ϕ^0, $K_{\phi,s}^0$, and $\Delta K_{\phi,s}^0$ have been used to discuss the nature of interactions present in the mixtures. The apparent molar expansivity ϕ_E^0 and its temperature derivative $(\partial\phi_E^0/\partial T)$ have also been calculated.



1. INTRODUCTION

Ionic liquids (ILs) are low-melting-point ionic compounds and have proven to be an excellent substitute for conventional molecular solvents due to their environmentally benign properties.[1−5] Amino acids are useful as starting material for the preparation of a wide range of ionic liquids, but the environment exerts an important influence over the conformational characteristics of amino acids. Proteins comprise polymers of α amino acids and play a central role in many cellular processes. Environmental changes and heat can disrupt the structure of proteins and induce denaturation which is a serious problem in the handling of proteins in drug manufacturing, food production, and biotransformation. Several schemes have been proposed aimed at protein stabilization[6−9] including using ionic liquid as a solvent.[10] The understanding of molecular level interactions among amino acids and ILs is essential in designing and optimization of a variety of novel processes in biotechnology and industry. In the current study, the solvation behavior of amino acids in aqueous IL solutions with variations in temperature and concentration has been analyzed. Various volumetric and compressibility parameters have been calculated to understand the influence of a series of amino acids upon ILs adequately. Some mixtures comprising ionic liquid and amino acid have also been studied successfully as reported in the literature.[11−16] In a previous work, we have reported the densities and speeds of sound of aqueous mixtures comprising ionic liquid and ester[17−20] and amino acids[21] to interpret the interaction behavior based on the structural characteristics of properties of the species involved. In the current study, an effort has been made to elucidate preferential interactions prevailing among amino acids and aqueous 1-ethyl-3-methyl imidazolium chloride [emim][Cl] mixtures. Various volumetric and compressibility parameters have been calculated to understand the mixing effects. Here, we have measured the experimental density and speed of sound of glycine, L-alanine, L-valine in aqueous [emim][Cl] solutions at temperature T = (288.15, 293.15, 298.15, 303.15, and 308.15) K. The speed of sound is considered to be a thermodynamic property when negligible[22] absorption of low frequency and low amplitude sound waves takes place as is the case in the present study. The data obtained from experimental measurements were used to determine apparent molar volume (V_ϕ), apparent molar adiabatic compressibility ($K_{\phi,s}$), partial molar volume (V_ϕ^0), and partial molar adiabatic compressibility ($K_{\phi,s}^0$). The limiting apparent molar expansivity ϕ_E^0, group contributions of V_ϕ^0 for amino acids, and hydration number were also calculated.

2. EXPERIMENTAL SECTION

2.1. Materials. 1-Ethyl-3-methyl imidazolium chloride, [emim][Cl] (Sigma Aldrich, USA; mass fraction > 0.97), glycine (Merck-Schuchardt, Germany, GC 0.99), L-alanine (Himedia, GC 99), and L-valine (Merck-Schuchardt, Germany, GC 0.99) have been used in this study. The water content as determined using Karl Fischer analysis was < 350 ppm after being vacuum dried at 70 °C overnight. The ionic liquid

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Table 1. Specification of Chemical Samples

chemical name	CAS No.	provenance	mass fraction purity
1-ethyl-3-methyl-imidazolium chloride	65039-09-0	Sigma-Aldrich, USA	> 0.97
glycine	56-40-6	Merck-Schuchardt	> 0.99
L-alanine	56-41-7	Himedia, India	0.99
L-valine	72-18-4	Merck-Schuchardt	0.99

[emim][Cl] was checked for any impurities by ^{1}H NMR (Bruker 300 MHz) and IR (ABB MB3000). All other details describing preparation of solutions have been given in our earlier studies.[17−21] Details of the chemicals used in the present study are also given in Table 1.

2.2. Density and Speed of Sound Measurements. Densities and speeds of sound of mixtures under investigation have been measured using Anton Paar DSA 5000 densimeter. The calibration and measurement details have been given in our earlier studies.[17−21] The temperature inside the densimeter was controlled to ± 0.01 K by a built in Peltier system. The precision in density and speed of sound measurements are $1\cdot10^{-3}$ kg·m^{-3} and $1\cdot10^{-2}$ m·s^{-1}, respectively. The full accuracies of all the factors involved in the density readings have been considered, and the uncertainty for the density was estimated to be 0.2 %. The standard uncertainty for the speeds of sound was estimated to be 3 m·s^{-1}. Measurements have been performed in triplicate to reproduce the results.

3. RESULTS AND DISCUSSION

3.1. Apparent Molar Quantities. Densities ρ and speeds of sound u at temperatures T = (288.15, 293.15, 298.15, 303.15, and 308.15) K for glycine, L-alanine, and L-valine in (0.0981 and 0.3003) mol·kg^{-1} aqueous [emim][Cl] solutions are reported in Table 2. The experimentally measured data have been used to calculate apparent molar volume V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ of amino acids, which were calculated from experimental density and speeds of sound data using the relations

$$V_\phi = M/\rho - 1000(\rho - \rho_0)/m\rho\rho_0 \quad (1)$$

$$K_{\phi,s} = M\kappa_s/\rho - \{1000(\kappa_{s,0}\rho - \kappa_s\rho_0)/m\rho\rho_0\} \quad (2)$$

$$\kappa_s = 1/(c^2\rho) \quad (3)$$

where m is the molality (mol·kg^{-1}) of amino acid in the ([emim][Cl] + water) mixture, M is the molar mass of the solute (kg·mol^{-1}) (amino acid) and ρ_0, $\kappa_{s,0}$, and ρ, κ_s are the densities (kg·m^{-3}) and coefficient of adiabatic compressibility (Pa^{-1}) for reference solvent (desired molality of aqueous [emim][Cl]) and (amino acid + [emim][Cl] + water) solutions, respectively. The obtained values of V_ϕ, and $K_{\phi,s}$ for amino acids in aqueous [emim][Cl] solutions are reported in Table 3. The V_ϕ values increase with the rise of temperature as well as with elongation of the alkyl chain length of amino acid. The trend of V_ϕ values with temperature follows as

288.15 K > 293.15 K > 298.15 K > 303.15 K > 308.15 K

The values of V_ϕ for glycine in 0.0981 mol·kg^{-1} aqueous solution of [emim][Cl] against molalities of glycine have been plotted in Figure 1 at different temperatures. The V_ϕ values as plotted in Figure 1 for all mixtures in the experimental temperature range are positive. The values of V_ϕ for amino acids in aqueous 0.0981 mol·kg^1 aqueous [emim][Cl] solutions increase with an increase in molar mass from glycine to L-alanine to L-valine.

Similar trends have been observed for L-alanine and L-valine at 0.0981 mol·kg^{-1} aqueous solution of [emim][Cl] against molalities. However, the V_ϕ values increase with the concentration of [emim][Cl] in 0.3003 mol·kg^{-1} aqueous solution of [emim][Cl] against molalities of amino acids but again retaining the same trend against temperature and chain length of amino acid as observed in 0.0981 mol·kg^{-1}[emim]-[Cl]. The negative values of $K_{\phi,s}$ as shown in Table 3 mean less compressibility of the mixture as compared to that of bulk. Moreover a decrease in magnitude of $K_{\phi,s}$ values with an increase in molality of amino acids suggests the presence of ion−dipole interactions.

3.2. Apparent Molar Properties at Infinite Dilution. Apparent molar volumes V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ varies with the molality of amino acids as represented by the following equations

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

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

where V_ϕ^0 and $K_{\phi,s}^0$ are apparent molar volume at infinite dilution, that is, partial molar volume and apparent molar adiabatic compressibility at infinite dilution, that is, partial molar adiabatic compressibility. The S_v and S_k are the experimental slopes which give an idea about the prevailing solute−solute interactions in the mixtures. The values of V_ϕ^0 and S_v collectively with $K_{\phi,s}^0$ and S_k obtained using least-squares fitting of V_ϕ and $K_{\phi,s}$ are given in Table 4 along with standard errors. The apparent molar properties at infinite dilution, the partial molar properties, give an idea about the presence of solute−solvent interactions. It is also observed from Table 4 that the positive V_ϕ^0 values at all concentrations follows the order L-valine > L-alanine > glycine.

The decrease in V_ϕ^0 values with an increase in [emim][Cl] molality represents the volume contraction[23] due to hydrophobic interactions. However the V_ϕ^0 values increase with a rise in temperature which suggests that at higher temperature significant solute−solvent interactions are present in the mixtures. Further, the higher V_ϕ^0 values are obtained for amino acids with a higher number of carbon atoms in the alkyl chain length. It is also suggested that partial molar volume is the volume comprising the molar volume of pure water and change in volume which occur due to interaction with water.

The variation of V_ϕ^0 of amino acids in aqueous [emim][Cl] are graphically represented in Figure 2 at different temperatures. The trend shown in Figure 2 shows that large values of V_ϕ^0 are observed for amino acids having longer alkyl chain length. The same behavior was also reported earlier.[24] The sign (positive) and magnitude (large) of the V_ϕ^0 values show the dominance of ion−dipole interactions over dipole−dipole interactions at high molalities of aqueous [emim][Cl] solutions. Positive S_v values for amino acids in aqueous and 0.3003 mol·kg^{-1} [emim][Cl] predict that (COO^-/NH_3^+) + IL interactions are predominant as compared to pair−pair interactions. The negative S_v values for amino acids in 0.0981 mol·kg^{-1} [emim][Cl] solutions predict that ion−solvent interactions prevail as compared to ion−ion interactions. This observed behavior results in a dehydrating effect upon amino acids. Further, with a rise in temperature a decrease in magnitude of $K_{\phi,s}^0$ values is observed. Less negative $K_{\phi,s}^0$ values are

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Table 2. Values of Densities ρ and Speeds of Sound c of Amino Acids in Aqueous Solutions of [emim][Cl] at Different Temperatures and Atmospheric Pressure

m	$\rho \cdot 10^{-3}$/kg·m^{-3}[b]					c/m·s^{-1}				
mol·kg^{-1}[a]	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
Glycine + 0.0981 mol·kg^{-1} [emim][Cl]										
0.0684	1.003954	1.002980	1.001750	1.000300	0.998624	1482.09	1497.35	1510.78	1520.12	1532.85
0.1185	1.005522	1.004530	1.003275	1.001820	1.000122	1485.45	1500.47	1513.71	1523.16	1535.16
0.2441	1.009478	1.008435	1.007135	1.005650	1.003910	1492.08	1507.13	1520.28	1531.04	1541.04
0.3745	1.013624	1.012530	1.011190	1.009680	1.007900	1499.20	1513.66	1526.54	1537.36	1547.36
0.4407	1.015750	1.014640	1.013265	1.011740	1.009940	1502.95	1517.65	1530.39	1541.21	1551.30
0.5737	1.020050	1.018890	1.017480	1.015920	1.014090	1507.69	1524.77	1537.27	1546.99	1557.46
0.6604	1.022880	1.021700	1.020250	1.018675	1.016810	1514.96	1529.14	1541.60	1551.23	1561.68
0.7894	1.027120	1.025900	1.024430	1.022800	1.020925	1522.95	1536.94	1549.15	1559.34	1569.22
0.9189	1.031440	1.030140	1.028650	1.026990	1.025100	1529.71	1543.24	1555.21	1564.34	1574.50
Glycine + 0.3003 mol·kg^{-1} [emim][Cl]										
0.0663	1.007190	1.006145	1.004830	1.003310	1.001575	1508.53	1522.12	1533.96	1544.20	1553.23
0.1303	1.009444	1.008370	1.007020	1.005480	1.003720	1512.57	1526.09	1537.94	1548.14	1556.54
0.2556	1.013720	1.012610	1.011190	1.009600	1.007780	1518.71	1531.96	1543.57	1553.51	1561.83
0.3705	1.017470	1.016320	1.014840	1.013220	1.011357	1525.53	1538.63	1550.07	1559.89	1568.03
0.4570	1.020199	1.019000	1.017500	1.015840	1.013950	1529.33	1542.30	1553.59	1563.27	1571.63
0.6063	1.024690	1.023480	1.021900	1.020190	1.018230	1538.19	1550.55	1561.55	1571.05	1579.13
0.6424	1.025730	1.024490	1.022935	1.021200	1.019220	1539.33	1552.53	1563.53	1573.04	1581.09
0.7973	1.030095	1.028800	1.027150	1.025370	1.023350	1548.34	1560.69	1571.42	1580.60	1588.18
0.8314	1.031029	1.029690	1.028080	1.026290	1.024260	1550.55	1562.57	1573.25	1582.45	1590.27
L-Alanine + 0.0981 mol·kg^{-1}[Emim][Cl]										
0.0505	1.003196	1.002220	1.000995	0.999540	0.997874	1481.68	1496.94	1510.28	1521.89	1531.86
0.1005	1.004564	1.003566	1.002310	1.000840	0.999160	1485.30	1500.48	1513.79	1525.26	1535.39
0.2143	1.007731	1.006679	1.005381	1.003870	1.002140	1492.88	1507.73	1520.75	1532.06	1541.76
0.2981	1.010110	1.009030	1.007680	1.006150	1.004400	1499.16	1513.82	1526.61	1537.74	1547.06
0.5017	1.016070	1.014910	1.013470	1.011850	1.010070	1513.53	1527.57	1539.89	1550.56	1559.64
0.6146	1.019430	1.018260	1.016780	1.015150	1.013320	1522.05	1535.80	1547.79	1558.04	1567.39
0.6768	1.021330	1.020140	1.018650	1.016980	1.015130	1526.79	1540.12	1551.91	1562.11	1570.81
0.8087	1.025420	1.024144	1.022670	1.020950	1.019100	1535.93	1549.13	1560.63	1570.53	1578.76
0.9612	1.030220	1.028910	1.027380	1.025628	1.023740	1545.00	1557.39	1569.61	1579.61	1589.64
L-Alanine + 0.3003 mol·kg^{-1}[emim][Cl]										
0.0666	1.006886	1.005845	1.004550	1.003043	1.001330	1509.47	1523.02	1534.82	1542.00	1551.04
0.1231	1.008640	1.007584	1.006270	1.004753	1.003028	1513.35	1526.72	1538.42	1546.00	1555.12
0.2619	1.012885	1.011790	1.010430	1.008884	1.007122	1522.85	1535.90	1547.26	1555.06	1563.00
0.3674	1.016055	1.014930	1.013530	1.011960	1.010162	1530.40	1543.17	1554.28	1561.60	1570.00
0.4540	1.018620	1.017460	1.016030	1.014435	1.012613	1536.75	1548.90	1559.78	1567.12	1575.66
0.5795	1.022285	1.021070	1.019594	1.017970	1.016100	1545.06	1557.21	1567.80	1575.07	1584.05
0.6228	1.023540	1.022299	1.020810	1.019170	1.017292	1548.12	1560.22	1570.65	1577.98	1586.81
0.7706	1.027736	1.026430	1.024900	1.023210	1.021260	1558.67	1570.31	1580.43	1587.11	1595.76
0.8437	1.029800	1.028460	1.026890	1.025180	1.023200	1563.70	1575.17	1585.11	1592.01	1600.55
L-Valine + 0.0981mol·kg^{-1} [emim][Cl]										
0.0552	1.003180	1.002210	1.000970	0.999514	0.997832	1484.02	1499.11	1512.03	1523.00	1533.49
0.0643	1.003406	1.002435	1.001185	0.999730	0.998043	1484.80	1500.01	1512.88	1524.03	1534.00
0.0951	1.004187	1.003201	1.001930	1.000470	0.998765	1488.55	1503.00	1516.00	1527.01	1537.02
0.1329	1.005160	1.004170	1.002875	1.001400	0.999680	1492.42	1507.15	1520.04	1530.80	1540.70
0.1742	1.006250	1.005240	1.003925	1.002440	1.000710	1497.00	1511.00	1524.00	1534.50	1544.50
0.2715	1.008905	1.007880	1.006520	1.005010	1.003255	1507.43	1521.45	1533.69	1544.23	1553.08
0.3658	1.011600	1.010560	1.009193	1.007640	1.005880	1518.05	1531.56	1543.37	1553.44	1561.85
0.4432	1.013900	1.012820	1.011490	1.009920	1.008121	1525.92	1539.06	1550.55	1560.31	1568.45
L-Valine + 0.3003 mol·kg^{-1} [emim][Cl]										
0.0378	1.006059	1.004985	1.003643	1.002123	1.000399	1504.97	1523.86	1533.60	1543.47	1555.13
0.0627	1.006865	1.005758	1.004382	1.002843	1.001113	1507.59	1526.40	1535.97	1545.75	1557.20
0.0959	1.007903	1.006758	1.005324	1.003783	1.002025	1511.08	1529.79	1539.13	1548.80	1559.95
0.1272	1.008847	1.007675	1.006207	1.004644	1.002864	1514.37	1532.99	1542.11	1551.67	1562.55
0.1641	1.009962	1.008733	1.007207	1.005621	1.003841	1518.25	1536.75	1545.62	1555.05	1565.61
0.2166	1.011502	1.010215	1.008632	1.006988	1.005178	1523.76	1542.11	1550.62	1559.87	1569.96
0.3620	1.015412	1.014050	1.012412	1.010774	1.009194	1539.05	1556.96	1564.46	1573.21	1582.02
0.4420	1.017492	1.016050	1.014492	1.012884	1.011534	1547.45	1565.13	1572.08	1580.54	1588.65

[a] m is the molality of amino acid. [b] The uncertainties $u(\rho)$ for the densities are estimated to be 0.2 % and uncertainties $u(c)$ in speeds of sound measurements are 3 m·s^{-1}. Standard uncertainties $u(T)$ in temperature measurements are 0.01 K.

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Table 3. Values of Apparent Molar Volumes V_ϕ and Apparent Molar Adiabatic Compressibility K_ϕ of Amino Acids in Aqueous Solutions of [emim][Cl] at Different Temperatures and Atmospheric Pressure

m	$V_\phi \cdot 10^6$/m^3·mol^{-1}					$K_\phi \cdot 10^6$/m^3·mol^{-1}·GPa^{-1}				
mol·kg^{-1}[a]	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 288.15	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
Glycine + 0.0981 mol·kg^{-1} [emim][Cl]										
0.0684	43.83	44.28	44.68	44.89	45.28	−45.02	−44.09	−43.34	−42.69	−42.12
0.1185	43.69	44.11	44.56	44.73	45.15	−45.37	−44.43	−43.68	−43.02	−42.45
0.2441	43.36	43.78	44.19	44.41	44.80	−45.75	−44.80	−44.04	−43.37	−42.79
0.3745	43.04	43.45	43.83	44.04	44.42	−46.01	−45.05	−44.28	−43.61	−43.03
0.4407	42.86	43.25	43.65	43.87	44.23	−46.12	−45.16	−44.39	−43.71	−43.13
0.5737	42.51	42.90	43.27	43.51	43.84	−46.35	−45.38	−44.60	−43.92	−43.33
0.6604	42.28	42.65	43.04	43.26	43.61	−46.48	−45.51	−44.73	−44.05	−43.46
0.7894	41.95	42.31	42.66	42.92	43.23	−46.68	−45.71	−44.92	−44.24	−43.65
0.9189	41.59	41.99	42.32	42.58	42.86	−46.89	−45.91	−45.12	−44.43	−43.83
Glycine + 0.3003 mol·kg^{-1} [emim][Cl]										
0.0663	38.90	39.20	39.82	40.20	40.74	−43.76	−43.02	−42.27	−41.71	−41.24
0.1303	39.22	39.59	40.18	40.53	41.01	−44.18	−43.43	−42.68	−42.11	−41.64
0.2556	39.79	40.12	40.70	41.08	41.57	−44.54	−43.78	−43.01	−42.45	−41.97
0.3705	40.33	40.67	41.23	41.58	42.04	−44.75	−43.99	−43.23	−42.65	−42.18
0.4570	40.71	41.10	41.60	41.98	42.41	−44.90	−44.14	−43.37	−42.79	−42.31
0.6063	41.40	41.71	42.23	42.60	43.05	−45.13	−44.36	−43.59	−43.01	−42.53
0.6424	41.57	41.92	42.37	42.76	43.22	−45.18	−44.42	−43.64	−43.06	−42.58
0.7973	42.23	42.58	43.06	43.44	43.87	−45.41	−44.64	−43.85	−43.27	−42.78
0.8314	42.36	42.75	43.17	43.54	43.97	−45.45	−44.68	−43.90	−43.31	−42.82
L-Alanine + 0.0981 mol·kg^{-1} [Emim][Cl]										
0.0505	61.81	62.48	62.94	63.35	63.71	−44.75	−43.82	−43.08	−42.42	−41.86
0.1005	61.60	62.17	62.73	63.11	63.47	−45.26	−44.32	−43.57	−42.91	−42.34
0.2143	61.11	61.64	62.13	62.53	62.96	−45.64	−44.69	−43.93	−43.27	−42.70
0.2981	60.73	61.22	61.76	62.13	62.52	−45.81	−44.86	−44.09	−43.43	−42.85
0.5017	59.79	60.25	60.77	61.19	61.51	−46.14	−45.18	−44.41	−43.74	−43.15
0.6146	59.35	59.75	60.24	60.61	60.96	−46.31	−45.35	−44.57	−43.90	−43.31
0.6768	59.06	59.46	59.93	60.33	60.68	−46.40	−45.44	−44.66	−43.98	−43.39
0.8087	58.48	58.93	59.30	59.71	60.01	−46.60	−45.63	−44.85	−44.17	−43.58
0.9612	57.86	58.27	58.65	59.03	59.34	−46.83	−45.85	−45.07	−44.38	−43.79
L-Alanine + 0.3003 mol·kg^{-1} [emim][Cl]										
0.0666	57.53	57.79	58.14	58.36	58.60	−43.75	−43.01	−42.26	−41.68	−41.22
0.1231	57.56	57.84	58.19	58.42	58.67	−44.13	−43.38	−42.63	−42.05	−41.58
0.2619	57.63	57.92	58.29	58.52	58.81	−44.50	−43.75	−42.99	−42.42	−41.94
0.3674	57.68	57.98	58.36	58.61	58.93	−44.69	−43.93	−43.17	−42.59	−42.12
0.4540	57.72	58.04	58.43	58.69	59.01	−44.82	−44.07	−43.30	−42.72	−42.25
0.5795	57.77	58.13	58.52	58.79	59.14	−45.01	−44.24	−43.47	−42.90	−42.42
0.6228	57.78	58.16	58.55	58.83	59.17	−45.07	−44.30	−43.53	−42.95	−42.47
0.7706	57.86	58.26	58.64	58.94	59.32	−45.27	−44.50	−43.72	−43.14	−42.66
0.8437	57.88	58.28	58.68	58.98	59.37	−45.36	−44.59	−43.81	−43.23	−42.75
L-Valine + 0.0981 mol·kg^{-1} [emim][Cl]										
0.0552	92.36	92.90	93.64	94.08	94.77	−44.83	−43.90	−43.16	−42.50	−41.94
0.0643	92.28	92.76	93.56	93.95	94.63	−44.96	−44.02	−43.28	−42.62	−42.06
0.0951	91.98	92.48	93.27	93.62	94.31	−45.23	−44.29	−43.54	−42.88	−42.31
0.1329	91.63	92.04	92.82	93.20	93.85	−45.41	−44.46	−43.71	−43.05	−42.48
0.1742	91.22	91.66	92.39	92.77	93.34	−45.54	−44.59	−43.83	−43.17	−42.60
0.2715	90.32	90.68	91.35	91.71	92.22	−45.75	−44.80	−44.04	−43.37	−42.79
0.3658	89.44	89.76	90.30	90.71	91.13	−45.91	−44.95	−44.19	−43.52	−42.94
0.4432	88.72	89.09	89.46	89.86	90.31	−46.03	−45.07	−44.30	−43.63	−43.05
L-Valine + 0.3003 mol·kg^{-1} [emim][Cl]										
0.0378	83.46	84.80	86.66	87.41	88.15	−43.21	−42.48	−41.74	−41.18	−40.72
0.0627	83.81	85.16	86.85	87.64	88.22	−43.71	−42.97	−42.22	−41.66	−41.19
0.0959	84.29	85.59	87.33	87.90	88.61	−44.00	−43.25	−42.49	−41.93	−41.46
0.1272	84.73	85.94	87.54	88.16	88.90	−44.15	−43.40	−42.64	−42.07	−41.60
0.1641	85.00	86.30	87.92	88.56	89.16	−44.28	−43.52	−42.76	−42.19	−41.71
0.2166	85.37	86.65	88.16	88.94	89.56	−44.41	−43.65	−42.88	−42.31	−41.83
0.3620	86.64	87.64	88.74	89.23	90.07	−44.67	−43.90	−43.12	−42.55	−42.08
0.4420	87.05	88.07	88.80	89.34	90.31	−44.78	−44.01	−43.23	−42.66	−42.19

[a] m is the molality of amino acid in the mixture of {[emim][Cl]+water} as solvent.

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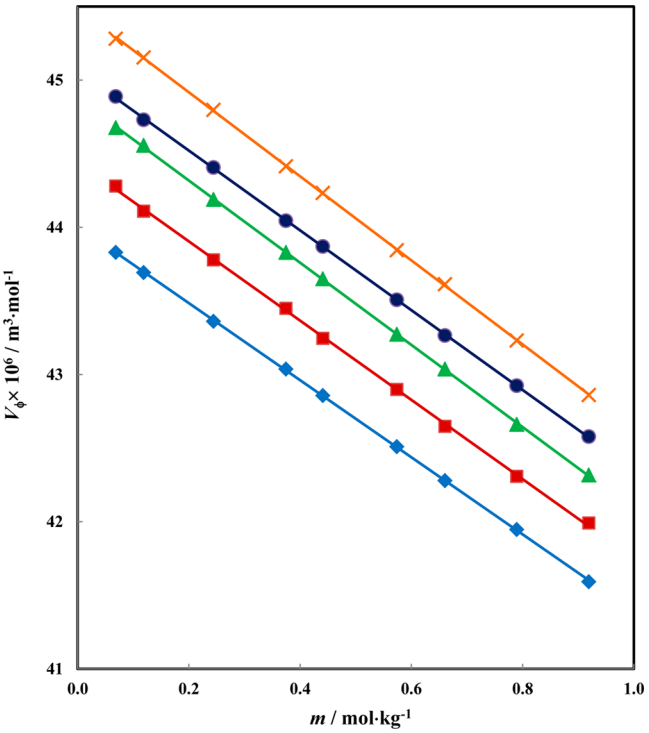

Figure 1. Apparent molar volume V_ϕ for glycine in 0.0981 mol·kg^{-1} [emim][Cl] at different temperatures against molalities m for glycine: blue ◆, 288.15 K; red ■, 293.15 K; green ▲, 298.15 K; purple ●, 303.15 K; orange ×, 308.15 K.

obtained for amino acids in aqueous [emim][Cl] solutions than amino acids in water, which makes the medium less compressible. The negative values of S_k suggest the solvation of ions due to weak ion−ion interactions, which is also evident from our S_v data.

3.3. Group Contributions of Standard Partial Molar Volume. A number of carbon atoms in the alkyl part of amino acids have a linear relationship with V_ϕ^0, which is represented using equation[25]

$$V_\phi^0 = V_\phi^0(NH_3^+, COO^-) + n_c V_\phi^0(CH_2) \quad (6)$$

where n_c is number of carbon atoms in the alkyl chain length of amino acids; $V_\phi^0(NH_3^+,COO^-)$ is the zwitterionic end group contribution and $V_\phi^0(CH_2)$ is the methylene group contribution toward V_ϕ^0 values.

($V_\phi^0(NH_3^+,COO^-)$ and $V_\phi^0(CH_2)$) are the zwitterionic end groups and methylene group contributions to V_ϕ^0, respectively. The least-squares regression analysis of equation 6 results in the $V_\phi^0(NH_3^+,COO^-)$ and $V_\phi^0(CH_2)$ values. The calculated values of $V_\phi^0(NH_3^+,COO^-)$ and $V_\phi^0(CH_2)$ have been reported in Table 5. The alkyl chain parts of the amino acids, that is, CH_2 of glycine, CH_3CH of L-alanine, and CH_3CH_3CHCH of L-valine have been studied here. The $V_\phi^0(CH_2)$ values are obtained from the mean of CH^- and CH_3^- groups contributions to the total V_ϕ^0 values of the amino acids. The following equations[26] have been used to calculate the other alkyl chains contributions:

$$V_\phi^0(CH_3) = 1.5V_\phi^0(CH_2) \quad (7)$$

$$V_\phi^0(CH) = 0.5V_\phi^0(CH_2) \quad (8)$$

From Table 5, it is observed that $V_\phi^0(NH_3^+,COO^-)$ values are large in comparison to $V_\phi^0(CH_2)$ values. This suggests that ion−ion interactions of [emim][Cl] ions and NH_3^+,COO^- groups dominate over [emim][Cl] hydrophobic interactions. The large $V_\phi^0(NH_3^+,COO^-)$ values in comparison to those of $V_\phi^0(CH_2)$ are mainly due to the molar mass difference of the respective groups and the contribution of a side group can result in increasing the V_ϕ^0 values.

3.4. Partial Molar Quantities of Transfer. Solute−solute interactions at infinite dilution are are not taken into consideration, therefore the nature of these interactions may be discussed using limiting molar quantities of transfer. The partial molar volumes of transfer ΔV_ϕ^0 and partial molar adiabatic compressibility of transfer $\Delta K_{\phi,s}^0$ of the amino acids from water to aqueous [emim][Cl] solutions were determined using the following equation:

$$\Delta Y_\phi^0 = Y_\phi^0 \text{ (in aqueous [emim][Cl] solution)} - Y_\phi^0 \text{ (in water)} \quad (9)$$

where Y_ϕ^0 represents V_ϕ^0 and $K_{\phi,s}^0$. The ΔV_ϕ^0 and $\Delta K_{\phi,s}^0$ values are reported in Table 6. The values of Y_ϕ^0 (in water) have been taken from our earlier work.[21] The values of ΔV_ϕ^0 as reported in Table 6 and plotted in Figure 3 show that the magnitude of ΔV_ϕ^0 values decreases at high [emim][Cl] concentrations. This is in contrast with the earlier reported behavior of amino acid+[Pmim][Br]+water[27] mixtures and amino acid+[Hmim]-[Cl]+water[28] mixtures. The values of ΔV_ϕ^0 are positive for amino acids in aqueous [emim][Cl] solutions except for L-valine in 0.3003 mol·kg^{-1} [emim][Cl] solutions. The positive $\Delta K_{\phi,s}^0$ values as reported in Table 6 decrease with an increase in temperature and [emim][Cl] concentration. The ΔV_ϕ^0 values provide partial information about the solute−solvent interactions[29−31] because solute−solute interactions contribute much less toward ΔV_ϕ^0 values. Depending upon the ΔV_ϕ^0 values, it is suggested that three types of interactions, (i) ion−ion interactions, (ii) ion-hydrophobic interactions, and (iii) hydrophobic−hydrophobic interactions, occur in amino acids + [emim][Cl] + water mixtures. Interactions between Cl^- and $[emim]^+$ ions of [emim][Cl] and (NH_3^+,COO^-) groups of amino acids, that is, ion−ion interactions result in positive values as per the cosphere overlap model[32] This occurs because the electrostriction is reduced and the structure of water becomes enhanced. Ion−hydrophobic interactions [interactions between Cl^- and $[emim]^+$ ions of [emim][Cl] and the nonpolar group of amino acids, and the $[emim]^+$ ion of [emim][Cl] and (NH_3^+,COO^-) group of amino acids] and also the hydrophobic−hydrophobic interactions between hydrophobic groups of amino acids and the alkyl part of the [emim][Cl] result in negative ΔV_ϕ^0 values as hydrophilic−hydrophobic and hydrophobic−hydrophobic group interactions have a greater tendency to occur because of the presence of an alkyl group, and also there will be a volume reduction due to co-sphere overlapping. The positive values of ΔV_ϕ^0 represent that due to hydrophilic−hydrophilic interactions, the expansion of volume takes place and some water molecules are released. Furthermore, the negative ΔV_ϕ^0 values for glycine and L-valine in 0.3003 mol·kg^{-1} [emim][Cl] solutions predict the dominance of interaction types (ii) and (iii) over type (i), that is, ion−ion interactions. The interaction between the alkyl part of imidazoline and nonpolar group of amino acids may lead to hydrophobic−hydrophobic interactions. Further, the intrinsic volume of solute and change in volume due to solute−solvent interactions is the actual standard partial molar volume.[33]

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Table 4. Values of Limiting Apparent Molar Volumes V_ϕ^0, Experimental Slopes S_v, Limiting Apparent Molar Adiabatic Compressibility K_ϕ^0, and Experimental Slope S_k, of Amino Acids in Aqueous Solutions of [emim][Cl] at Different Temperatures

m^a	T	$V_\phi^0 \cdot 10^6$	$S_v \cdot 10^6$	$K_\phi^0 \cdot 10^6$	$S_k \cdot 10^6$
mol·kg $^{-1}$	K	m^3 mol^{-1}	$m^3 \cdot kg$ $mol^{-3/2}$	m^3 mol^{-1} GPa^{-1}	kg m^3 mol^{-2} GPa^{-1}
			Glycine		
0.0981	288.15	44.01(±0.004)	−2.62(±0.008)	−45.13(±0.084)	−2.03(±0.156)
	293.15	44.44(±0.011)	−2.69(±0.020)	−44.19(±0.082)	−1.98(±0.151)
	298.15	44.88(±0.005)	−2.79(±0.010)	−43.45(±0.080)	−1.93(±0.148)
	303.15	45.06(±0.005)	−2.71(±0.009)	−42.79(±0.078)	−1.89(±0.143)
	308.15	45.49(±0.005)	−2.85(±0.009)	−42.22(±0.078)	−1.86(±0.144)
0.3003	288.15	38.63(±0.018)	4.53(±0.034)	−43.89(±0.092)	−2.00(±0.173)
	293.15	38.96(±0.026)	4.57(±0.048)	−43.15(±0.089)	−1.96(±0.168)
	298.15	39.59(±0.022)	4.35(±0.041)	−42.39(±0.088)	−1.92(±0.166)
	303.15	39.96(±0.017)	4.36(±0.032)	−41.83(±0.087)	−1.89(±0.165)
	308.15	40.47(±0.012)	4.25(±0.022)	−41.37(±0.087)	−1.86(±0.163)
			L-Alanine		
0.0981	288.15	62.03(±0.014)	−4.37(±0.025)	−45.03(±0.115)	−2.01(±0.207)
	293.15	62.63(±0.035)	−4.62(±0.062)	−44.09(±0.113)	−1.97(±0.202)
	298.15	63.17(±0.018)	−4.75(±0.032)	−43.35(±0.111)	−1.92(±0.200)
	303.15	63.57(±0.017)	−4.76(±0.031)	−42.69(±0.109)	−1.89(±0.196)
	308.15	63.96(±0.015)	−4.85(±0.028)	−42.12(±0.108)	−1.86(±0.193)
0.3003	288.15	57.50(±0.006)	0.46(±0.011)	−43.88(±0.088)	−1.89(±0.169)
	293.15	57.75(±0.006)	0.65(±0.012)	−43.14(±0.087)	−1.85(±0.166)
	298.15	58.10(±0.007)	0.70(±0.013)	−42.38(±0.086)	−1.82(±0.164)
	303.15	58.31(±0.006)	0.81(±0.011)	−41.81(±0.087)	−1.81(±0.167)
	308.15	58.55(±0.007)	1.00(±0.014)	−41.34(±0.087)	−1.79(±0.166)
			L-Valine		
0.0981	288.15	92.87(±0.007)	−9.39(±0.027)	−44.89(±0.092)	−2.84(±0.380)
	293.15	93.39(±0.027)	−9.84(±0.111)	−43.95(±0.090)	−2.78(±0.372)
	298.15	94.27(±0.014)	−10.83(±0.06)	−43.21(±0.089)	−2.72(±0.366)
	303.15	94.65(±0.009)	−10.81(±0.038)	−42.56(±0.087)	−2.67(±0.362)
	308.15	95.38(±0.020)	−11.55(±0.081)	−41.99(±0.087)	−2.63(±0.358)
0.3003	288.15	83.39(±0.119)	8.73(±0.513)	−43.61(±0.160)	−3.05(±0.690)
	293.15	84.79(±0.119)	7.83(±0.515)	−42.86(±0.156)	−2.82(±0.673)
	298.15	86.76(±0.156)	5.28(±0.672)	−42.11(±0.154)	−2.55(±0.663)
	303.15	87.49(±0.160)	4.77(±0.690)	−41.55(±0.153)	−2.33(±0.658)
	308.15	88.09(±0.119)	5.45(±0.511)	−41.09(±0.152)	−2.12(±0.653)

[a] m is the molality of [emim][Cl].

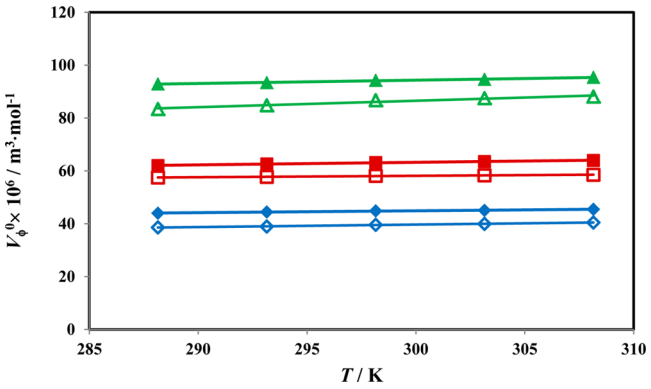

Figure 2. Apparent molar volume at infinite dilution, V_ϕ^0 for glycine (blue ◆,◇), L-alanine (red ■,□), and L-valine (green ▲,△) in aqueous solutions of [emim][Cl] (filled symbols, 0.0981 mol·kg^{-1} [emim][Cl]; empty symbols, 0.3003 mol·kg^{-1} [emim][Cl]) at different temperatures.

The intrinsic volume has two major contributions:[34]

$$V_{\text{intrinsic}} = V_{\text{vw}} + V_{\text{void}} \quad (10)$$

Table 5. Contributions of the Zwitterionic Group (NH_3^+ COO^-), CH_2 Group, and Other Alkyl Chains to the Infinite Dilution Apparent Molar Volume V_ϕ^0 in Aqueous [emim][Cl] Solutions at 298.15 K

	$V_\phi^0 \cdot 10^6$/m^3 mol^{-1}	
group	m_{IL} = 0.1019 mol·kg^{-1}	m_{IL} = 0.3042 mol·kg^{-1}
($NH_3^+COO^-$)	29.329	25.260
CH_2–	16.332	15.524
CH_3CH–	32.665	31.049
$(CH_3)_2CHCH$–	65.330	66.044

where V_{vw} is the van der Waals volume occupied by the solute[35] and V_{void} is the volume associated with the voids and abandoned spaces present. Equation10 has been modified by Shahidi et al.[36] to include the solute contribution to its standard partial molar volume as

$$V_\phi^0 = V_{\text{vw}} + V_{\text{void}} - \sigma_s \quad (11)$$

where σ_s is the shrinkage in volume due to interactions of water molecules with hydrogen bonding groups of solute molecules. So, the partial molar volume can be represented as

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Table 6. Partial Molar Volume of Transfer, ΔV_ϕ^0 and Partial Molar Isentropic Compressibility of Transfer, $\Delta K_{\phi,s}^0$ of Amino Acids in Aqueous Solutions of [emim][Cl] at Different Temperatures

m^a	T	$\Delta V_\phi^0 \cdot 10^6$	$\Delta K_{\phi,s}^0 \cdot 10^6$
mol·kg^{-1}	K	m^3·mol^{-1}	m^3·mol^{-1}·GPa^{-1}
		Glycine	
0.0981	288.15	2.30	−1.241
	293.15	2.50	−1.046
	298.15	2.77	−1.051
	303.15	2.75	−0.967
	308.15	2.95	−0.853
0.3003	288.15	−3.08	0.574
	293.15	−2.98	0.404
	298.15	−2.52	0.273
	303.15	−2.35	0.174
	308.15	−2.07	0.163
		L-Alanine	
0.0981	288.15	4.77	−0.0322
	293.15	5.15	−0.191
	298.15	5.47	−0.311
	303.15	5.63	−0.397
	308.15	5.80	−0.408
0.3003	288.15	0.24	1.120
	293.15	0.27	0.766
	298.15	0.40	0.651
	303.15	0.37	0.483
	308.15	0.39	0.373
		L-Valine	
0.0981	288.15	4.36	−0.390
	293.15	4.68	−0.544
	298.15	5.32	−0.657
	303.15	5.47	−0.740
	308.15	5.93	−0.748
0.3003	288.15	−5.12	0.890
	293.15	−3.92	0.546
	298.15	−2.09	0.441
	303.15	−1.69	0.262
	308.15	−1.36	0.157

[a] m is the molality of [emim][Cl].

$$V_\phi^0 = V_{vw} + V_{void} - V_{shrinkage} \quad (12)$$

where V_{vw} and V_{void} are assumed to be the same in aqueous and aqueous [emim][Cl] solutions, therefore the overall positive ΔV_ϕ^0 values of the amino acids justify the decrease in the $V_{shrinkage}$ in the [emim][Cl] solutions and vice versa for glycine and L-valine in 0.3003 mol·kg^{-1}[emin][Cl] solutions.

3.5. Hydration Number. Hydration number (n_H) for glycine, L-alanine, and L-valine in aqueous [emim][Cl] solutions was estimated using the following equation[37]

$$n_H = \frac{V_{\phi(e)}^0}{V_e^0 - V_b^0} \quad (13)$$

where V_e^0 is the molar volume of electrostricted water and V_b^0 is the molar volume of the bulk water. The value of $(V_e^0 - V_b^0)$ is approximately −3.0 cm^3 mol^{-1} for electrolytes at 298.15 K.[38] The $V_{\phi(e)}^0$ values were calculated using the following equation[39]

$$V_{\phi(e)}^0 = V_\phi^0 - V_{int}^0 \quad (14)$$

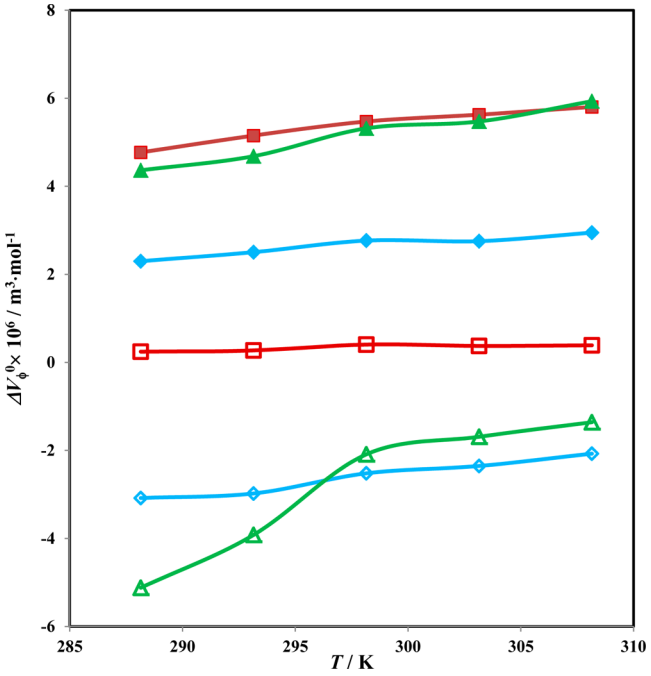

Figure 3. Plot of apparent molar volume of transfer against temperature for glycine (blue ◆,◇), L-alanine (red ■,□), and L-valine (green ▲,△) in aqueous solutions of [emim][Cl] (filled symbols, 0.0981 mol·kg^{-1} [emim][Cl]; empty symbols, 0.3003 mol·kg^{-1} [emim][Cl]) at different temperatures.

where V_{int}^0 is the intrinsic partial molar volume. V_{int}^0, the intrinsic partial molar volume, includes van der Waals volume, and volume due to packing effects. The values of V_{int}^0 for amino acids were calculated with the help of molar crystal volumes using the relationship[40]

$$V_{int}^0 = \frac{0.7}{0.634} V_\phi^0(\text{cryst}) \quad (15)$$

where 0.7 and 0.634 are the packing densities for the molecules in an organic crystal and for randomly packed spheres, respectively. The crystal densities of amino acids give by Berlin and Pallansch[41] were used to calculate crystal molar volumes at 298.15 K. The calculated n_H values are reported in Table 7. It is observed from Table 7 that n_H values for the amino acids follow the order: n_H (L-alanine) > n_H (L-valine) > n_H (glycine) in all aqueous [emim][Cl] solutions except in 0.3003 mol·kg^{-1} [emim][Cl] solutions where it follow the order: n_H (L-valine) > n_H (L-alanine) > n_H (glycine). Also, n_H values increase overall as the concentration of aqueous [emim][Cl] increases. This shows that there is a decrease in the electrostriction of water thereby increasing amino acids + IL interactions with increasing [emim][Cl] concentrations which suggests strong interactions at higher [emim][Cl] concentrations[42] in present mixtures.

3.6. Thermal Expansion Coefficients. The thermal expansion coefficient α was determined using the relationship[43]

$$\alpha = 1/V_\phi^0(\partial V_\phi^0/\partial T) \quad (16)$$

The solute−solvent interactions[44] can be interpreted with the help of α values reported in Table 8 at 298.15 K. The values of α graphically represented in Figure 4 exhibit an overall increase as the concentration of aqueous [emim][Cl] increases, except for L-valine which suggests a volume expansion or decrease in

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Table 7. Hydration Number (n_H) of Amino Acids in Aqueous [emim][Cl] Solutions at 298.15 K

	n_H		
amino acid	m_{IL} = 0.0000 mol·kg^{-1}	m_{IL} = 0.0981 mol·kg^{-1}	m_{IL} = 0.3003 mol·kg^{-1}
glycine	3.85	2.12	3.72
L-alanine	5.49	2.60	4.14
L-valine	5.73	2.37	4.64

Table 8. Limiting Apparent Molar Expansivity ϕ_E^0, Coefficient of Thermal Expansion α, and Temperature Derivative of Limiting Apparent Molar Expansivity $(\partial^2 V_\phi^0/\partial T^2)$ at T = 298.15 K

m^a	$\phi_E^0 \cdot 10^6$	$\alpha \cdot 10^3$	$(\partial^2 V_\phi^0/\partial T^2)$
mol·kg^{-1}	m^3·mol^{-1}·K^{-1}	K^{-1}	m^3·mol^{-1}
	Glycine		
0.0000	0.0404	2.643	0.0002
0.0981	0.0716	2.869	−0.0015
0.3003	0.0934	3.070	0.0005
	L-Alanine		
0.0000	0.0449	2.631	0.0001
0.0981	0.0959	2.919	−0.0032
0.3003	0.0528	2.972	−0.0010
	L-Valine		
0.0000	0.0469	2.585	0.0006
0.0981	0.1256	2.208	−0.0004
0.3003	0.2422	2.435	−0.0162

[a] m is the molality of [emim][Cl].

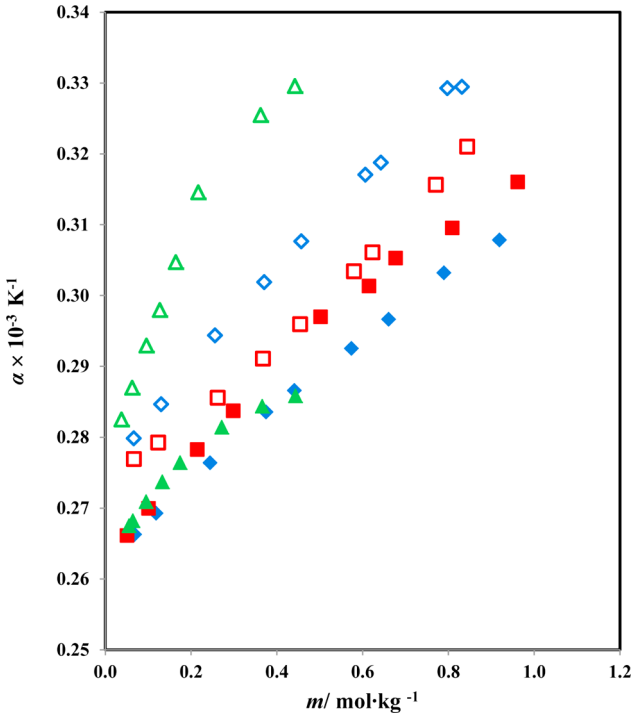

Figure 4. Coefficient of thermal expansion α against concentration of amino acids: glycine (blue ◆,◇), L-alanine (red ■, □), and L-valine (green ▲,△) in aqueous solutions of [emim][Cl] (filled symbols, 0.0981 mol·kg^{-1} [emim][Cl]; empty symbols, 0.3003 mol·kg^{-1} [emim][Cl]) at different temperatures.

compressibility of the solutions when molecules of amino acid are added in the aqueous [emim][Cl] solutions.

3.7. Limiting Apparent Apparent Molar Expansivities.

Limiting apparent molar expansivity ϕ_E^0 was determined using equation:

$$\phi_E^0 = (\partial V_\phi^0/\partial T) \quad (17)$$

The calculated values of ϕ_E^0 are reported in Table 8. The limiting apparent molar expansivity was also represented as a combination[45] of two terms:

$$\phi_E^0 = \phi_E^0(\text{elect}) + \phi_E^0(\text{str}) \quad (18)$$

where ϕ_E^0(elect) and ϕ_E^0(str) are expansivities due to electrostriction and solvent structure changes, respectively. The expansivity due to electrostriction changes ϕ_E^0(elect) dominates at higher temperature, whereas expansivity due to structural changes ϕ_E^0(str) dominates at lower temperatures. The temperature derivative of ϕ_E^0, $(\partial\phi_E^0/\partial T)$, was also obtained using

$$(\partial\phi_E^0/\partial T) = (\partial^2 V_\phi^0/\partial T^2) \quad (19)$$

The $(\partial\phi_E^0/\partial T)$ values as reported in Table 8 are found to be negative for all mixtures. The values have been found negative for all mixtures. The sign of the temperature derivative of limiting apparent molar expansivity predicts whether the solutes have structure making or breaking characteristics upon mixing with solvent.[43,46] Therefore it predicts amino acid to be a possible structure breaker. Further, the overall negative values of $(\partial\phi_E^0/\partial T)$ suggest the dominance of ϕ_E^0(elect) over ϕ_E^0(str) toward the prediction of solute−solvent interactions in amino acids + [emim][Cl] + water mixtures studied in this work.

4. CONCLUSION

Density and speeds of sound values at different temperatures have been reported for amino acids + [emim][Cl] + water mixtures in this study. Experimental data have been used to determine apparent molar properties, partial molar properties, and partial molar properties of transfer. The results shows that values of V_ϕ^0 decrease with an increase in concentrated aqueous [emim][Cl] solutions due to hydrophobic interactions or caging effect of water molecules leading to volume contraction. The results obtained from compressibility data ($K_{\phi,s}^0$ and $\Delta K_{\phi,s}^0$ values) support the results obtained from apparent molar volume. Also, strong interactions among the [emim][Cl] ions and the zwitterionic group of amino acid have been confirmed by their large $V_\phi^0(NH_3^+,COO^-)$ values as compared to $V_\phi^0(CH_2)$ values. The obtained values of ΔV_ϕ^0 values suggest the presence of hydrophobic−hydrophobic interactions between the alkyl part of [emim]$^+$ and the nonpolar groups of amino acids.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: palchem21@gmail.com.

Notes

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