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Temperature Dependence of Physical Properties of Amino Acid Ionic Liquid Surfactants

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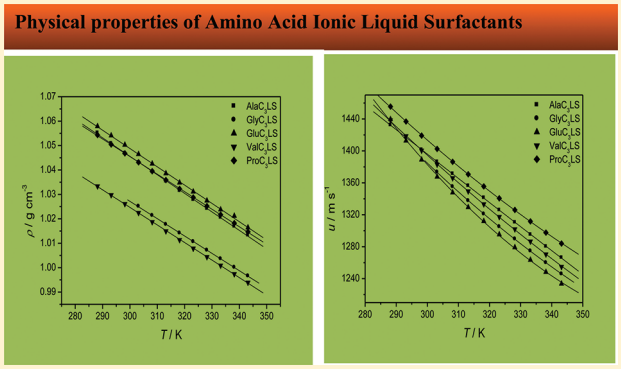
Supporting Information

ABSTRACT: The density (ρ), speed of sound (u), and refractive index (n_D) of amino acid ionic liquid surfactants (AAILSs) prepared from natural amino acids, L-glycine, L-alanine, L-valine, L-glutamic acid, and L-proline, and sodium lauryl sulfate have been measured in the temperature range from (288.15 to 343.15) K. The temperature dependence of density has been used to calculate the coefficient of thermal expansion (α). Using the experimental ρ and u values, the isentropic compressibility (κ_s) has been calculated for various AAILSs. The molar refraction (R_M) has been calculated from experimental n_D values in the temperature range from (288.15 to 343.15) K. Refractive indices of ILs were found higher than those of normal organic liquids but are comparable to long hydrocarbon chain organic solvents.



1. INTRODUCTION

Room temperature ionic liquids (ILs), exhibiting unique physicochemical properties, are rapidly gaining interest as greener replacements for traditional volatile organic solvents in various chemical processes and have been the focus of many scientific investigations.[1−12] Further, the modulating nature of ILs has widened their applications and utilities in many areas of chemistry. The physical and derived properties of pure ILs are of immense importance for their better and selective use in various chemical processes. The physical properties such as density, speed of sound, and refractive index address the questions related to bulk scale features, and the systematic measurement of such physical properties enables us to settle useful structure−property relationships for the ILs, stressing the nature of ions and the substituent effects. The properties of ILs such as thermal expansion, isentropic compressibility, and molar refraction derived from the experimental data of density, speed of sound, and refractive index are important in understanding the nature of inter- or intramolecular forces. Therefore, various researchers have measured the physical properties of neat ILs.[13−21]

Depending upon the choice of anion or cation, one can design surface active amphiphilic ILs. Such ILs have shown surface active properties which are different and better than those from conventional surfactants, thus emerging as a superior class of surfactants.[22−27] ILs surfactants used so far, though "green" in terms of negligible vapor pressure, generally contain synthetic quaternary nitrogen cations such as alkylammonium, dialkylimidazolium, or pyridinium with anions having halogen atoms such as Cl or F and release HCl or HF by hydrolysis under certain conditions which may cause environmental hazards when released through wastewater effluents.[28−30] Therefore, toxicity and biodegradation remain central issues while dealing with ILs, and the quest for synthesis of more greener ILs in terms of toxicity and biodegradability is increasing day by day.[31] In this regard, several researchers have synthesized and characterized the biobased ILs.[32−34]

This work presents the temperature dependence of physical properties such as density, speed of sound, and refractive index of relatively greener, biodegradable, and nontoxic amino acid ionic liquid surfactants (AAILS's) based on natural amino acids and sodium lauryl sulfate whose synthesis and applications have been reported by us in a recent communication.[35] Important secondary properties such as isothermal expansion, isentropic compressibility, and molar refraction of AAILS's have also been derived from the primary data. Useful structure−property correlations have been settled for various physical and derived properties.

2. EXPERIMENTAL SECTION

2.1. Materials. AAILS's were synthesized and characterized as described in one of our recent communications.[35] In brief, the natural amino acids (L-glycine, L-alanine, L-valine, L-glutamic acid, and L-proline) and sodium lauryl sulfate (SLS) all having a purity of >0.99 mass fraction, were obtained from Sisco Research Labortories Pvt. Ltd., Mumbai, and used as precursors. The structures of the chemicals are given in Table 1. In the first step of synthesis of AAILSs, the amino acid ester

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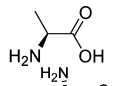
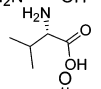
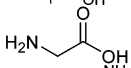
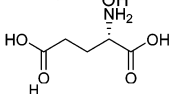
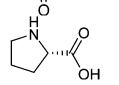
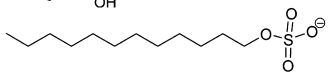
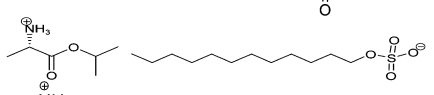
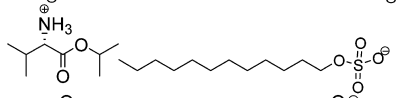
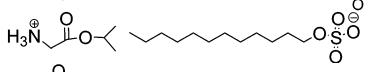
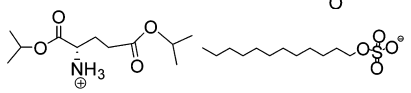
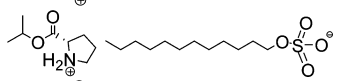
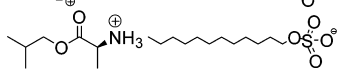
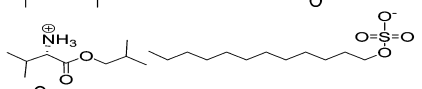
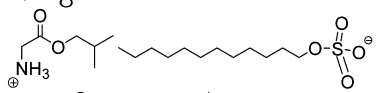
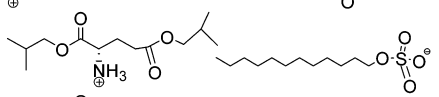
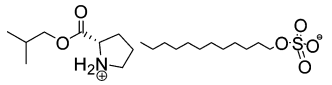
Table 1. Schematic Molecular Structure of the Chemicals and Synthesized Amino Acid Ionic Liquid Surfactants

Compounds	Acronym	Molecular Structure
L-Alanine	Ala	
L-valine	Val	
L-glycine	Gly	
L-glutamic acid	Glu	
L-Proline	Pro	
Sodium lauryl sulphate	SLS	
L-Alanine isopropylester lauryl sulphate	$AlaC_3LS$	
L-Valine isopropylester lauryl sulphate	$ValC_3LS$	
L-glycine isopropylester lauryl sulphate	$GlyC_3LS$	
L-glutamic acid diisopropylester lauryl sulphate	$GluC_3LS$	
L-Proline isopropylester lauryl sulphate	$ProC_3LS$	
L-Alanine isobutylester lauryl sulphate	$AlaC_4LS$	
L-Valine isobutylester lauryl sulphate	$ValC_4LS$	
L-Glycine isobutylester lauryl sulphate	$GlyC_4LS$	
L-Glutamic acid diisobutylester lauryl sulphate	$GluC_4LS$	
L-Proline isobutylester lauryl sulphate	$ProC_4LS$	

hydrochlorides (AAECls) were prepared using amino acids, thionyl chloride, and isopropyl or isobutyl alcohol at 0 °C. In the next step, equimolar amounts of AAECls and SLS were then dissolved in hot water. After the completion of the reaction, water was removed under vacuum, and AAILS's were extracted by the addition of dichloromethane. Henceforth, we will use general symbols to represent the amino acids and use the number of carbon atoms to represent the alkyl groups of ester, say, glycine propyl ester lauryl sulfate, as $GlyC_3LS$. Prior to measurements all of the AAILSs were further purified according to the procedure described elsewhere.[12] ILs were dried and degassed in vacuum at 70 °C for 48 h. Karl Fisher analysis of the samples indicated the moisture content to be less than 0.04 mass %. The estimated purity from various analyses was found to be ≥0.98 mass fraction. All of the AAILS's were kept in vacuum desiccators to avoid contact from atmospheric air. The structure and name of the synthesized AAILSs are given in Table 1. NMR, FTIR, and mass spectra of synthesized AAILS's are given in the Supporting Information.

2.2. Density and Speed of Sound Measurements. Density (ρ) and speed of sound (u) measurements for various AAILS's were carried out using an Anton Paar (model DSA 5000) vibrating tube density meter with a resolution of $5{\cdot}10^{-6}$ $g{\cdot}cm^{-3}$ and 0.01 $m{\cdot}s^{-1}$. The temperature of the apparatus was controlled to within ± 0.01 K by a built-in Peltier device that corresponds to an uncertainty in density of ± 0.0002 %. To prevent the uncertainty in the density readings from being affected by the sample viscosity, a number of corrections are needed. Such corrections rely on both the availability of experimental viscosity data over the pressure and temperature ranges considered and the use of properly defined and evaluated damping equations. The deviations between the viscosity corrected and noncorrected density data can climb up from 0.5 to 1 % for lower temperatures. In light of the full accuracies of all factors involved in the density readings, an accuracy of $\pm\ 1{\cdot}10^{-5}$ $g{\cdot}cm^{-3}$ for the raw density data is assumed. The values reported in this work are noncorrected density data. The overall uncertainty in comparison with literature data for the calibrating liquids and in the averaged density measure-

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Table 2. Experimental Densities (ρ) and Speed of Sound (u) for Various AAILS's in the Temperature Range (288.15 to 343.15) K

T	ρ	u	ρ	u	ρ	u	ρ	u	ρ	u
K	g·cm^{-3}	m·s^{-1}	g·cm^{-3}	m·s^{-1}	g·cm^{-3}	m·s^{-1}	g·cm^{-3}	m·s^{-1}	g·cm^{-3}	m·s^{-1}
	$AlaC_3LS$		$GlyC_3LS$		$GluC_3LS$		$ValC_3LS$		$ProC_3LS$	
288.15	1.05522	1432.3			1.0579	1439.7	1.03335	1438.4	1.05433	1455.5
293.15	1.05089	1416.7			1.05411	1412.8	1.02974	1418.5	1.05045	1436.8
298.15	1.04687	1401.4			1.05031	1389.0	1.02611	1400.5	1.04680	1419.2
303.15	1.04307	1386.3	1.02514	1373.4	1.04647	1367.6	1.02244	1382.9	1.04315	1402.4
308.15	1.03922	1371.3	1.02137	1355.1	1.04257	1347.9	1.01871	1365.9	1.03952	1386.3
313.15	1.03531	1356.3	1.01768	1337.6	1.03860	1329.5	1.01493	1349.4	1.03589	1370.7
318.15	1.03147	1341.3	1.01416	1320.9	1.03481	1312.0	1.01136	1333.2	1.03227	1355.5
323.15	1.02782	1325.9	1.01065	1305.0	1.03113	1295.3	1.00786	1317.4	1.02873	1340.6
328.15	1.02417	1310.4	1.00714	1289.6	1.02746	1279.2	1.00437	1301.9	1.02522	1326.0
333.15	1.02052	1295.2	1.00363	1274.6	1.02379	1263.5	1.00088	1286.6	1.02170	1311.7
338.15	1.01689	1280.2	1.00012	1259.9	1.0212	1248.3	0.99739	1270.4	1.01820	1297.6
343.15	1.01323	1266.3	0.99658	1245.8	1.01644	1233.6	0.9939	1254.9	1.01469	1284.0
	$AlaC_4LS$		$GlyC_4LS$		$GluC_4LS$		$ValC_4LS$		$ProC_4LS$	
288.15	1.04918	1447.6					1.01682	1434.4	1.04322	1460.2
293.15	1.04548	1423.6					1.01298	1421.3	1.03954	1445.2
298.15	1.04175	1401.9					1.00929	1408.6	1.03588	1429.2
303.15	1.03802	1381.6	1.01362	1372.1			1.00572	1394.6	1.03222	1413.0
308.15	1.03413	1362.5	1.00988	1355.2			1.00215	1379.9	1.02857	1397.2
313.15	1.03013	1343.9	1.00614	1339.0			0.99857	1365.5	1.02492	1381.5
318.15	1.02631	1325.8	1.00238	1323.0			0.99499	1350.9	1.02127	1366.1
323.15	1.02260	1308.1	0.99871	1307.6	1.01445	1330.6	0.99195	1335.5	1.01772	1349.1
328.15	1.01908	1291.2	0.99515	1292.5	1.01078	1314.4	0.98781	1318.1	1.01421	1332.9
333.15	1.01560	1275.8	0.99189	1277.6	1.00713	1299.9	0.98423	1299.9	1.01085	1316.8
338.15	1.01214	1261.0	0.98822	1263.0	1.00354	1284.2	0.98080	1275.0	1.00761	1301.5
343.15	1.00875	1246.6	0.98453	1248.7	1.00000	1270.5	0.97808	1249.5	1.00498	1286.2

Table 3. Correlations for the Densities (ρ), Speed of Sound (u), and Refractive Indices (n_D) of Different AAILS's as a Function of Temperature

	ρ		u			
AAILS	g·cm^{-3}	SD/σ	m·s^{-1}	SD/σ	n_D	SD/σ
$AlaC_3LS$	$1.2731 - 7.586\cdot10^{-4}\ (T/K)$	$3.09\cdot10^{-4}$	$2304.3 - 3.0(T/K)$	0.4	$1.544-3.1\cdot10^{-4}$	$1.1\cdot10^{-4}$
$GlyC_3LS$	$1.2755 - 7.5579\cdot10^{-4}\ (T/K)$	$1.80\cdot10^{-4}$	$3331.0 - 9.4(T/K) + 0.01(T/K)^2$	0.6	$1.627-5.3\cdot10^{-4}$	$2.9\cdot10^{-4}$
$GluC_3LS$	$1.2734 - 7.4898\cdot10^{-4}\ (T/K)$	$3.94\cdot10^{-4}$	$15610 - 122(T/K) + 0.36(T/K)^2 - 3.5(T/K)^3$	0.4	$1.553-3.3\cdot10^{-4}$	$1.2\cdot10^{-4}$
$ValC_3LS$	$1.2403 - 7.1899\cdot10^{-4}\ (T/K)$	$1.84\cdot10^{-4}$	$3067.5 - 7.6\ (T/K) + 0.07(T/K)^2$	0.8	$1.541-3.1\cdot10^{-4}$	$1.5\cdot10^{-4}$
$ProC_3LS$	$1.2603 - 7.1863\cdot10^{-4}\ (T/K)$	$1.60\cdot10^{-4}$	$3219.8 - 8.7(T/K) + 0.01(T/K)^2$	0.5	$1.550-3.2\cdot10^{-4}$	$1.9\cdot10^{-4}$
$AlaC_4LS$	$1.2628 - 7.4197\cdot10^{-4}\ (T/K)$	$3.18\cdot10^{-4}$	$4119.4 - 14.0(T/K) + 0.01(T/K)^2$	0.6	$1.574-4.1\cdot10^{-4}$	$0.8\cdot10^{-4}$
$GlyC_4LS$	$1.2361 - 7.3398\cdot10^{-4}\ (T/K)$	$2.30\cdot10^{-4}$	$3331.0 - 9.4(T/K) + 0.01(T/K)^2$	0.6	$1.659-6.5\cdot10^{-4}$	$0.4\cdot10^{-4}$
$GluC_4LS$	$1.2524 - 7.3640\cdot10^{-4}\ (T/K)$	$1.38\cdot10^{-4}$	$2272.4 - 2.9(T/K)$	0.7	$1.575-3.9\cdot10^{-4}$	$0.8\cdot10^{-4}$
$ValC_4LS$	$1.2209 - 7.09727\cdot10^{-4}(T/K)$	$3.06\cdot10^{-4}$	$17098 - 150.6(T/K) + 0.49(T/K)^2 - 5.4(T/K)^3$	1.1	$1.551-3.3\cdot10^{-4}$	$1.0\cdot10^{-4}$
$ProC_4LS$	$1.2462 - 7.0593\cdot10^{-4}\ (T/K)$	$4.19\cdot10^{-4}$	$2378.3 - 3.2(T/K)$	0.5	$1.606-4.9\cdot10^{-4}$	$0.7\cdot10^{-4}$

ments of liquids is judged to be less than 0.02 %. The reproducibility of the results was confirmed by performing the measurements in triplicate.

2.3. Refractive Index Measurements. The refractive index was measured using a Mettler-Toledo (Model RE-40 D) refractrometer having a high resolution optical sensor. Measurements were made with a resolution and limit of error $\pm\ 1\cdot10^{-4}$. The temperature of the apparatus was controlled to within $\pm$ 0.1 K by a built-in Peltier device. Dried and degassed samples kept in desiccators were directly injected through a syringe in the measuring cell. The reproducibility of the results was confirmed by performing at least three experiments for each sample in the whole temperature range.

3. RESULTS AND DISCUSSION

3.1. Density (ρ) and Speed of Sound (u). Experimental values of ρ and u for the various AAILS's as a function of temperature are given in Table 2. The temperature dependence of density, speed of sound, and refractive index was correlated by means of a polynomial type equation:

$$F(Q) = \sum_{i=1}^{n} A_i T^{i-1} \tag{1}$$

where Q represents the properties measured in general (ρ, u, and n_D) and T represents the temperature. Correlations of ρ and u as a function of temperature along with the standard deviations are given in Table 3. ρ values for various AAILSs as a function of temperature have been plotted and shown in Figure

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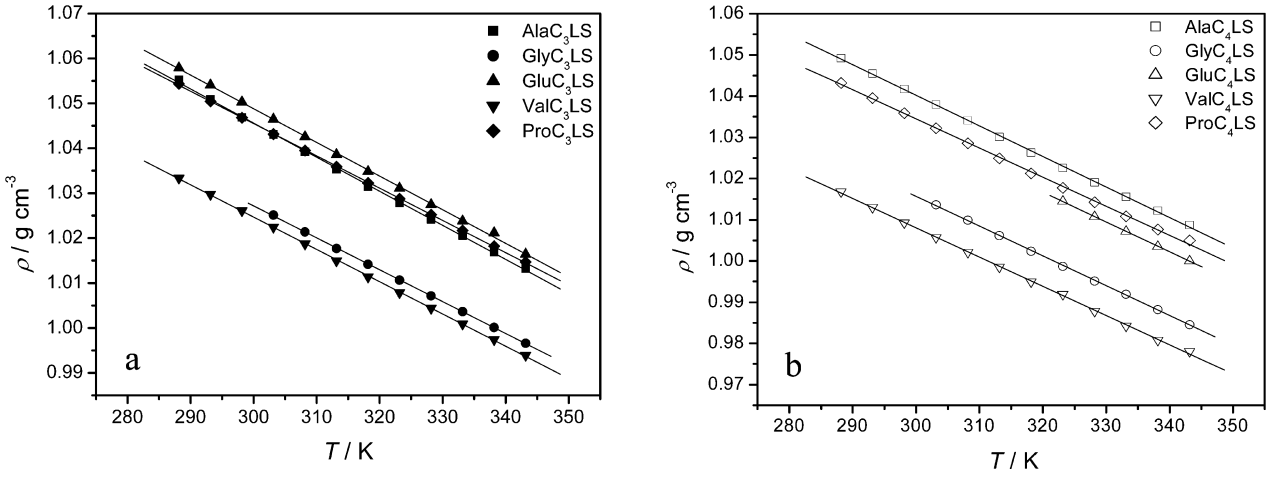

Figure 1. Variation of density of various AAILS's as a function of temperature: (a) propyl analogues; (b) butyl analogues.

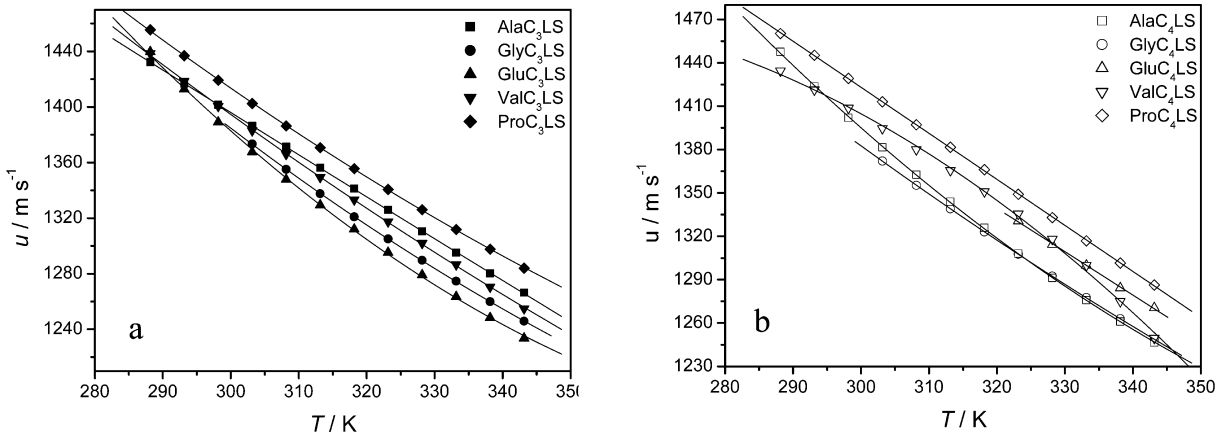

Figure 2. Temperature dependence of speed of sound for various AAILSs: (a) propyl analogues; (b) butyl analogues.

Table 4. Estimated Values of Isentropic Compressibility ($10^{12}\ \kappa_S$), of Different AAILSs as a Function of Temperature

T/K	$AlaC_3LS$	$GlyC_3LS$	$GluC_3LS$	$ValC_3LS$	$ProC_3LS$	$AlaC_4LS$	$GlyC_4LS$	$GluC_4LS$	$ValC_4LS$	$ProC_4LS$
288.15	461.9		456.0	467.7	447.7	454.8			478.0	449.6
293.15	474.1		475.3	482.7	461.1	472.0			488.7	460.9
298.15	486.4		493.5	496.9	474.3	488.4			499.3	472.6
303.15	498.8	517.2	510.9	511.4	487.4	504.7	524.0		511.3	485.2
308.15	511.7	533.2	528.0	526.1	500.6	520.9	539.2		524.0	498.1
313.15	525.1	549.2	544.7	541.1	513.8	537.5	554.4		537.1	511.2
318.15	538.9	565.1	561.4	556.3	527.2	554.3	569.9		550.8	524.7
323.15	553.4	581.0	578.1	571.7	540.9	571.5	585.7	556.8	565.2	539.9
328.15	568.64	597.0	594.8	587.4	554.7	588.6	601.6	572.7	582.7	555.0
333.15	584.2	613.3	611.9	603.6	568.9	605.0	617.7	587.6	601.3	570.5
338.15	600.0	629.9	628.4	621.2	583.3	621.4	634.4	604.2	627.2	585.9
343.15	615.5	646.5	646.5	638.9	597.8	638.0	651.5	619.5	654.9	601.5

1a,b. The ρ of the ILs decreases linearly with the rise of temperature for all of the investigated AAILS's. The ρ of the AAILS's was found to be dependent on the nature of cation and varies in the order: $GluC_3LS > AlaC_3LS \approx ProC_3LS > GlyC_3LS > ValC_3LS$ for the propyl derivatives of amino acid cations in AAILS's, whereas for the butyl analogues, the ρ follows the order: $AlaC_4LS > ProC_4LS > GluC_4LS > GlyC_4LS > ValC_4LS$. It was observed that the AAILSs having a propyl group are slightly denser than that of their butyl analogues. Extra free volume created by the bulkier butyl group may be responsible for comparatively lower densities of AAILSs having butyl derivative.

Since the temperature dependence of ρ is linear for the AAILSs, density values as a function of temperature were used to calculate the coefficient of thermal expansion, α, which is defined by the following equation:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial \ln \rho}{\partial T}\right)_P \quad (2)$$

where V and ρ are the volume and density of AAILS's, respectively. α values for various AAILS's calculated from eq 2

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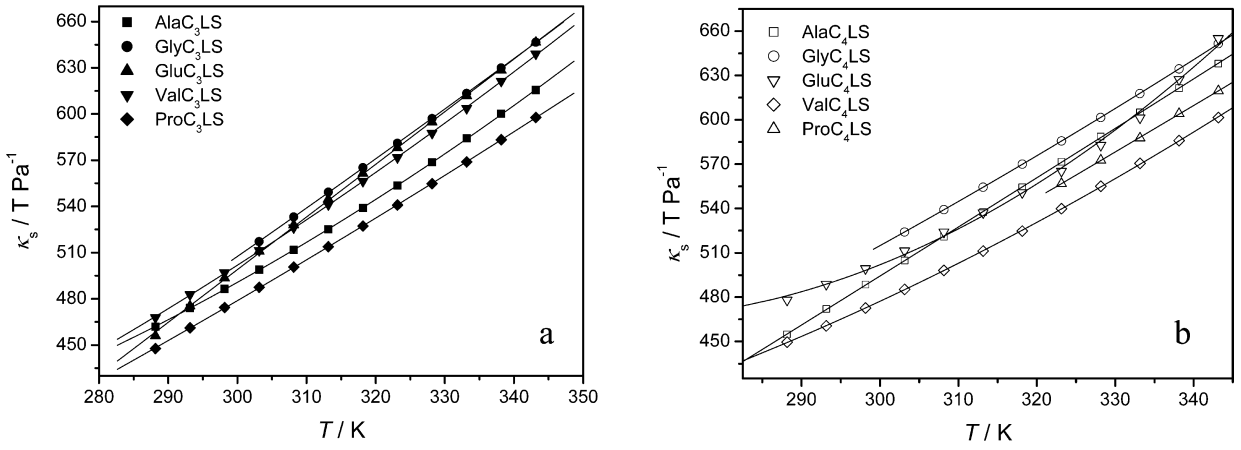

Figure 3. Temperature dependence of isentropic compressibility for various AAILSs: (a) propyl analogues; (b) butyl analogues.

Table 5. Experimental Values of Refractive Indices (n_D) and Calculated Values of Molar Refraction (R_M) of Various AAILS's at Different Temperatures

T/K	n_D	R_M	n_D	R_M	n_D	R_M	n_D	R_M	n_D	R_M
	$AlaC_3LS$		$GlyC_3LS$		$GluC_3LS$		$ValC_3LS$		$ProC_3LS$	
288.15	1.4542	102.04			1.4575	128.21	1.4555	111.83	1.4575	109.24
293.15	1.4525	102.13			1.4559	128.28	1.4541	111.93	1.4559	109.32
298.15	1.4512	102.27			1.4542	128.33	1.4527	112.03	1.4542	109.34
303.15	1.4498	102.37	1.4630	100.92	1.4528	128.46	1.4514	112.15	1.4525	109.37
308.15	1.4480	102.39	1.4603	100.79	1.4509	128.47	1.4495	112.15	1.4510	109.44
313.15	1.4466	102.50	1.4576	100.66	1.4493	128.57	1.4483	112.31	1.4492	109.44
318.15	1.4449	102.54	1.4549	100.51	1.4476	128.61	1.4465	112.31	1.4478	109.53
323.15	1.4434	102.60	1.4529	100.49	1.4461	128.70	1.4450	112.37	1.4461	109.54
328.15	1.4418	102.64	1.4497	100.23	1.4442	128.68	1.4434	112.41	1.4446	109.60
333.15	1.4404	102.73	1.4465	99.97	1.4429	128.81	1.4419	112.47	1.4432	109.68
338.15	1.4387	102.75	1.4441	99.86	1.4410	128.66	1.4403	112.51	1.4414	109.67
343.15	1.4371	102.79	1.4414	99.69	1.43920	128.80	1.4388	112.57	1.4398	109.70
	$AlaC_4LS$		$GlyC_4LS$		$GluC_4LS$		$ValC_4LS$		$ProC_4LS$	
288.15	1.4560	106.61					1.4568	117.68	1.4648	115.90
293.15	1.4540	106.58					1.4555	117.84	1.4623	115.77
298.15	1.4520	106.55					1.4538	117.89	1.4598	115.64
303.15	1.4500	106.53	1.4624	107.87			1.4519	117.88	1.4574	115.52
308.15	1.4479	106.50	1.4592	107.63			1.4505	117.99	1.4549	115.39
313.15	1.4458	106.48	1.4560	107.38			1.4488	118.01	1.4524	115.25
318.15	1.4437	106.43	1.4527	107.10			1.4471	118.05	1.4500	115.13
323.15	1.4418	106.42	1.4494	106.82	1.4472	138.46	1.4455	118.04	1.4477	115.02
328.15	1.4397	106.35	1.4462	106.54	1.4453	138.45	1.4438	118.15	1.4452	114.86
333.15	1.4377	106.29	1.4430	106.22	1.4432	138.38	1.4422	118.21	1.4427	114.68
338.15	1.4354	106.17	1.4397	105.93	1.4414	138.39	1.4406	118.25	1.4401	114.46
343.15	1.4336	106.14	1.4365	105.65	1.4393	138.30	1.4390	118.20	1.4378	114.24

were as ($AlaC_3LS$ = 7.33, $GlyC_3LS$ = 7.29, $GluC_3LS$ = 7.22, $ValC_3LS$ = 7.09, $ProC_3LS$ = 6.95, $AlaC_4LS$ = 7.21, $GlyC_4LS$ = 7.31, $GluC_4LS$ = 7.22, $ValC_4LS$ = 7.11, $ProC_4LS$ = 6.90)·10^{-4} K^{-1}. This indicates that the AAILS's do not expand appreciably in the studied temperature range. α for all of the investigated AAILS's was found (6.9 to 7.3)·10^{-4} K^{-1}, which is considerably less than the molecular organic liquids but higher than classical molten salts. α for the investigated AAILS's is slightly higher than that of imidazolium-based ILs.[13,14] For the molten salts like molten NaCl, very high electrostatic interactions renders $\alpha \approx 3.0$ which is quite less than that of AAILS's which possesses hydrogen bonding and weak electrostatic interactions. α showed very weak dependency on the nature of amino acid or on the nature of their derivatization (propyl and butyl analogues in AAILSs).

Speed of sound (u) as a function of temperature for investigated AAILS's is shown in Figure 2a,b. u decreases with the increase in temperature for the investigated AAILS's. From the measured u and ρ data, isentropic compressibility, κ_s, was estimated using the relation:

$$\kappa_S = 1/u^2\rho \tag{3}$$

The calculated values of κ_s are given in Table 4. As can be seen from Figure 3a,b, κ_s for the investigated AAILS's increases with the increase in temperature. AAILS's studied here are less compressible than organic liquids as expected due to presence of Coloumbic interactions between the ions. However, the κ_s of AAILS's is higher as compared to the imidazolium-based ILs.[13,14] Higher κ_s of AAILS's may be because of more free

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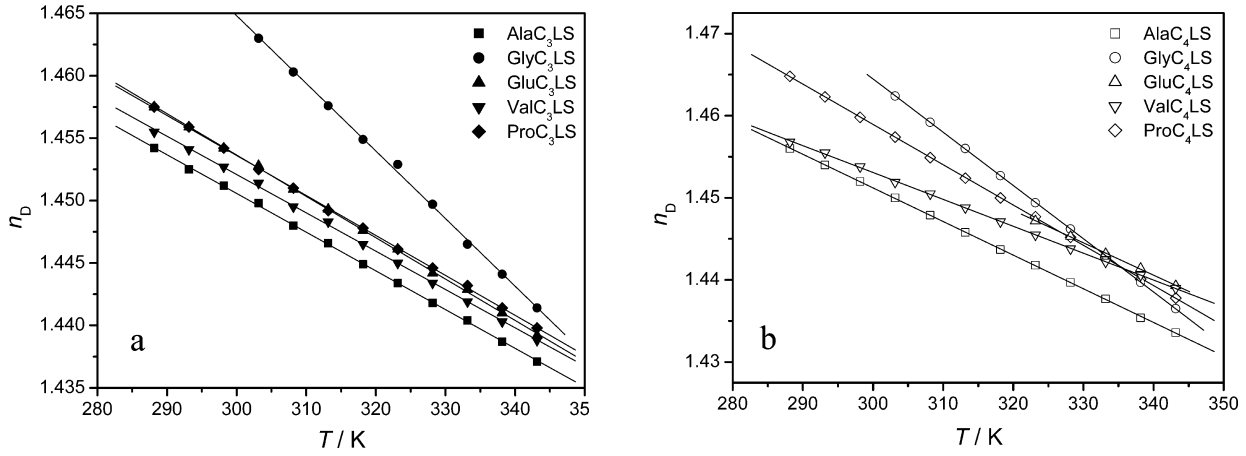

Figure 4. Variation of refractive index for various AAILS's as a function of temperature: (a) propyl analogues; (b) butyl analogues.

volume due to the large alkyl chain length of anion and bulky headgroup. κ_s followed the order: $GlyC_3LS$ > $ValC_3LS$ > $GluC_3LS$ > $AlaC_3LS$ > $ProC_3LS$, and a similar order was followed by butyl analogues of AAILSs. κ_s did not change much by derivatization (propyl or butyl) of amino acid cation.

3.2. Refractive Indices. Experimental results of temperature dependence of refractive indices n_D for different AAILS's are presented in Table 5 and are shown in Figure 4a,b. Correlations for the temperature dependence of n_D are given in Table 2. The refractive indices n_D of the AAILSs studied lie in the range (1.454 to 1.465) at room temperature which is comparable to imidazolium-based ILs or typical long-chain organic solvents such as hexadecane (1.433) and dodecanol (1.441).[13,14,36] This small variation in n_D for the investigated AAILS's shows the negligible dependency of n_D on the nature of cation of AAILSs. n_D decreases in a linear manner with the increase in temperature for all of the investigated AAILS. $GluC_3LS$ and $GluC_4LS$ show comparatively higher changes in n_D with the temperature when compared to other homologous AAILS's. n_D of AAILSs was found to be dependent on the nature of cation and varies in the order: $AlaC_3LS$ > $ValC_3LS$ > $GluC_3LS$ ≈ $ProC_3LS$ > $GlyC_3LS$. A similar series is observed for butyl derivatives of amino acid cations. Since molar properties are more informative, we calculated molar refraction R_M values for these liquids using the Lorentz−Lorenz relationship

$$R_M = \left(\frac{M}{\rho}\right)\left(\frac{n_D^2 - 1}{n_D^2 + 2}\right) \quad (4)$$

where all of the symbols have their usual meaning. Equation 4 is equivalent to,

$$R_M = N\alpha/3\varepsilon_0 \quad (5)$$

where N is the Avogadro number, α is the mean molecular polarizability ($\alpha = 4\pi\varepsilon_0 a^3$, a is the sphere radius), and ε_0 is the permittivity of free space. From eq 5, R_M can be interpreted as the hard core volume, that is, an approximate measure of the total volume (without free space) of molecules in one mole of the compound. R_M values are given in Table 5. R_M for the AAILS's having propyl derivatives of amino acid cation follows the order: $GlyC_3LS$ > $AlaC_3LS$ > $ProC_3LS$ > $ValC_3LS$ > $GluC_3LS$, whereas for the butyl analogue, it varies as $AlaC_4LS$ > $GlyC_4LS$ > $ProC_4LS$ > $ValC_4LS$ > $GluC_4LS$ at room temperature.

■ ASSOCIATED CONTENT

Supporting Information

Chemical analysis of synthesized AAILSs. This material is available free of charge via the Internet at http://pubs.acs.org.

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