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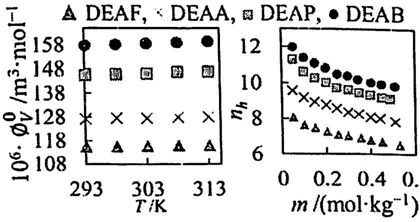
Density and Speed-of-Sound Measurements for Dilute Binary Mixtures of Diethylammonium-Based Protic Ionic Liquids with Water

Shrikant P. Musale, Kunal R. Patil, Rajshree J. Gavhane, and Dilip H. Dagade*

Department of Chemistry, Shivaji University, Kolhapur 416004, India

Supporting Information

ABSTRACT: Physicochemical properties of diethylammonium (DEA)-based protic ionic liquids and their aqueous solutions were obtained using experimental measurements of density (ρ) at different temperatures from T = (293.15 to 313.15) K and the speed of sound (w) at 298.15 K. Four DEA-based protic ionic liquids (PILs) with carboxylates as anions were synthesized. The standard entropy (S^0) and lattice potential energy (U_{POT}) for pure PILs were estimated from molecular volumes at 298.15 K obtained using experimental density data. Apparent molar volumes (ϕ_V), isobaric expansivity (α), isentropic compressibility (β_S), and isothermal compressibility (β_T) have been obtained for aqueous solutions of PILs using experimental density and speed-of-sound data. These data have been further used to understand the electrostriction and concentration dependence of internal pressure. The Passynski method has been used to estimate concentration-dependent hydration numbers of PILs. The results obtained have been discussed in terms of concentration- and temperature-dependent hydrophobic hydration, hydrophobic ion association, water structural changes, and so on. It has been observed that hydrophobic hydration persists in the entire studied concentration and temperature ranges. A critical examination of the data and results obtained reveals that the studied bio-ionic liquids can act as potential candidates in the pharmaceutical industry and in protein chemistry.



1. INTRODUCTION

Ionic liquids (ILs) have already attracted the attention of the scientific community due to their unique properties. Protic ionic liquids (PILs) are another class of ILs which are easily synthesized in high purity by the combination of a Brønsted acid and a Brønsted base. The unique feature of PILs is that they have an available proton on the cation which is responsible for hydrogen bonding, so they strongly interact with polar solvents.[1] The researchers showed a keen interest in the use of PILs as catalysts for organic synthesis,[2,3] biological applications,[4] self-assembly media,[5,6] electrolytes in fuel cells,[7] and industrial applications.[8] The multitude of applications for protic ionic liquids was excellently reviewed by Greaves et al.[9] This review focused on the use of PILs for specific applications and the need to know the properties of ionic liquids when mixed with an additional solvent or solute. Limiting the use of ionic liquids as an alternative to traditional organic solvents are the toxicity and expensive production cost of ILs. To overcome these limitations, researchers are in a continuous search to synthesize "bio-ionic liquids",[10,11] which are defined as ionic liquids made up of solely biomaterials, i.e., both the cation and anion constituents are of biological origin (either naturally occurring or from the metabolites of biochemical processes existing in living organisms). The ammonium-based PILs to some extent decrease the window of limitations, as they are low-toxicity and low-cost alternatives from the applications perspective. In the dissolution of polymers, separation processes, and organic synthesis, ammonium-based ionic liquids play a major role.[12−14] To diversify the applications of ammonium-based PILs and to know the intermolecular interactions with the solvent, the physiochemical properties of aqueous solutions of PILs must be studied. Ammonium-based PILs such as diethylethanolammonium,[15] *n*-butylammonium,[16] and triethylammonium[17] have been studied to provide reliable thermodynamic data and to know the interactions between PILs and solvent. As new protic ionic liquids are emerging at high rates, sufficient thermodynamic data is needed to know the interactions between PILs and various solvents. In our laboratory, the ion–ion and ion–solvent interactions in aqueous solutions of ionic liquids have been studied previously using vapor pressure osmometric,[18−20] volumetric, and speed-of-sound measurements for aqueous solutions of ionic liquids.[17,18,21,22] Considering the importance of bio-ionic liquids and the need for thermophysical data as outlined above, we report in this article the thermodynamic properties of pure diethylammonium-based carboxylate ionic liquids and their aqueous solutions. For this, four PILs were synthesized with diethylammonium (DEA) as a cation and an aliphatic carboxylate (RCOO⁻ where R = $-H$, $-CH_3$, $-CH_2CH_3$, and $-CH_2CH_2CH_3$) as an anion. The resultant PILs are diethylammonium formate [DEAF], diethylammonium acetate [DEAA], diethylammonium propionate [DEAP], and diethylammonium butanoate [DEAB]. The density of these PILs and their aqueous solutions has been

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Table 1. Chemical Name, CAS No., Molecular Mass, Water Content, Mass Fraction Purity, and Source of Chemicals Used

chemical name	CAS no.	molecular mass (g·mol^{-1})	water content (mass fraction)	mass fraction purity	source
diethylamine[a]	109-89-7	73.14		≥0.99	Merck
formic acid[a]	64-18-6	46.03		≥0.95	Sigma-Aldrich
acetic acid[a]	64-19-7	60.05		≥0.99	SD Fine Chemicals
propanoic acid[a]	79-09-4	74.08		≥0.99	Merck
butanoic acid[a]	107-92-6	88.11		≥0.98	Merck
diethylammonium formate[b]		119.17	0.0043	≥0.98	synthesized in lab
diethylammonium acetate[b]		133.19	0.0054	≥0.98	synthesized in lab
diethylammonium propionate[b]		151.22	0.0025	≥0.97	synthesized in lab
diethylammonium butanoate[b]		161.25	0.0027	≥0.99	synthesized in lab

[a]Used as received without further purification. [b]The purity of synthesized PILs was estimated by ^{1}H NMR spectra analysis. Water content in synthesized PILs, estimated using the Karl Fischer titration method, was taken into consideration for the preparation of aqueous PIL solutions.

measured from T = (293.15 to 313.15) K in the concentration range of (~0.02 to ~0.5) mol·kg^{-1}. The standard entropy (S^0) and lattice potential energy (U_{POT}) of pure PILs were estimated at 298.15 K. The experimental density and speed-of-sound data obtained for aqueous solutions of studied PILs have been used to estimate the apparent molal volume (ϕ_V), partial molal volumes of solvent ($\bar{V}_1$) and solute ($\bar{V}_2$), isobaric expansivity (α), isentropic compressibility (β_S), isothermal compressibility (β_T), and so on. The Passynski method[23] is used to calculate the concentration-dependent hydration number (n_h) of the studied PILs. The results obtained were discussed in terms of the ionic hydration, hydrophobic interactions, water structural changes, effects of alkyl chain length, temperature variation for physiochemical properties, and so on.

2. EXPERIMENTAL SECTION

2.1. Materials. The chemicals used in this work are listed in Table 1 with the source and mass fraction purity. Chemicals received from commercial manufacturers were used without any further purification.

2.2. Synthesis of PILs. The synthesis of diethylammonium formate and diethylammonium acetate was carried out by using reported methods.[24,25] Diethylammonium propionate and diethylammonium butanoate were synthesized by a similar procedure. The dropwise addition of a stoichiometric quantity of carboxylic acids such as formic acid, acetic acid, propanoic acid, and butanoic acid was made in the round-bottomed flask containing diethylamine which was kept in a recirculating, heated water bath and fixed with a reflux condenser with constant stirring at 333.15 K for 1 h and then at 343.15 K for 2 h to complete the reaction and form diethylammonium formate [DEAF], diethylammonium acetate [DEAA], diethylammonium propionate [DEAP], and diethylammonium butanoate [DEAB]. Synthesized PILs were dried at 343.15 K for 2 days under vacuum in the presence of P_2O_5. The ^{1}H NMR spectra are given in the Supporting Information (Figures S1–S4). The purities of the synthesized PILs were confirmed with ^{1}H NMR (see Supporting Information) and are reported in Table 1. Furthermore, the pH-metric titration of aqueous PILs showed the absence of any unreacted component in the final product. Karl Fischer titration was carried out to find the water content (Table 1) in synthesized PILs, which was taken into consideration during the preparation of the solutions. All aqueous solutions of PILs were prepared on a molality basis and converted to a molarity scale whenever necessary using experimental density data. Quartz doubly distilled water was used for the preparation of solutions. A Mettler Toledo ML204/A01 balance with a readability of 0.1 mg was used for weighing.

2.3. Density Measurements. The density of pure PILs and their aqueous solutions in the concentration range (~0.02 to ~0.5) mol·kg^{-1} was determined from T = (293.15 313.15) K using an Anton PAAR (DMA60/602) digital densitometer. The temperature constancy of the vibrating tube was better than ±0.02 K as it was maintained around the sample cell of the densitometer using a Julabo F34-HE with a temperature accuracy and stability of ±0.01 K. By applying the humidity and laboratory pressure corrections, the uncertainties in the density measurements were found to be on the order of ±2 × 10^{-2} kg·m^{-3}. The uncertainty in the density data has been obtained in the following way. Using known densities of water and air at a given temperature, instrumental constants A and B were obtained using the equation $d = A + B\tau^2$, where τ is the oscillation period of the vibrating tube of a densitometer. For this, at least 15 readings were taken after the thermal equilibration for each sample of known densities, i.e., water and air (the air densities used for calibration were humidity and lab-pressure corrected). The standard deviations in τ values were obtained and used to estimate the uncertainties in instrumental constants A and B which were in turn were used to obtain the uncertainties in the measured densities of aqueous solutions of ionic liquids using the method of propagation errors. Uncertainties in the density data thus obtained and the uncertainty in concentration were further used to determine the uncertainties in the derived properties such as the apparent molar volumes, partial molar volumes, excess molar volumes, and so forth using the method of propagation of errors. The estimated uncertainty data are reported along with the density and volume properties tabulated below in the Results section. Further details about calibration, testing, and error analysis for density measurements were also reported earlier.[18,21,22,26]

2.4. Speed-of-Sound Measurements. The speed-of-sound measurements of aqueous solutions of PILs at 298.15 K in the concentration range of (~0.05 to ~0.5) mol·kg^{-1} were made using an ultrasonic interferometer operating at a 2 MHz frequency (M/S Mittle Enterprises). The constant temperature of (298.15 ± 0.02) K was achieved by circulating water inside the cell of an interferometer by means of a Julabo F34-HE cryostat having a temperature accuracy and stability of ±0.01 K. Each speed-of-sound measurement reported here for each sample is the average over at least 10 readings. Using the repeated (at least 10 separate measurements) speed-of-sound measurements for pure liquid water at 298.15 K, the standard deviation in the speed of sound was found to be better than ±0.5 m·s^{-1}. This standard deviation and the uncertainties in

Table 2. Data of Experimental Density (ρ), Molar Volume (V_m), and Molecular Volume (V_{molc}) over the Temperature Range from T = (293.15 to 313.15) K and at Standard Entropy (S^0), and Lattice Potential Energy (U_{POT}) for PILs at 298.15 K and at Ambient Pressure of 94.4 kPa[a]

T/K	ρ/kg·m^{-3}	10^6V_m/m^3·mol^{-1}	V_{molc} /nm^3	S^0/J·K^{-1}·mol^{-1}	U_{POT}/kJ·mol^{-1}	T/K	ρ/kg·m^{-3}	10^6V_m/m^3·mol^{-1}	V_{molc} /nm^3	S^0/J·K^{-1}·mol^{-1}	U_{POT}/kJ·mol^{-1}
		DEAF						DEAA			
293.15	1028.05	115.91	0.1925			293.15	1008.95 (1220.00)[d]	132.01	0.2192		
298.15	1020.45 (1039.00)[b] (990.00)[c]	116.78	0.1939	271.2	602.4	298.15	1002.79 (958.00)[e] (1021.40)[f]	132.82	0.2205	304.4	590.3
303.15	1015.75	117.32	0.1948			303.15	993.36 (1016.52)[f]	134.08	0.2226		
308.15	1011.37	117.83	0.1957			308.15	989.81 (1011.87)[f]	134.56	0.2234		
313.15	1006.98	118.34	0.1965			313.15	986.31	135.04	0.2242		
		DEAP						DEAB			
293.15	986.04	153.36	0.2546			293.15	965.08	167.08	0.2774		
298.15	979.72	154.35	0.2563	349.0	576.9	298.15	958.77	168.18	0.2793	377.6	569.5
303.15	970.30	155.85	0.2588			303.15	949.51	169.82	0.2820		
308.15	966.60	156.45	0.2598			308.15	945.80	170.49	0.2831		
313.15	962.95	157.04	0.2608			313.15	942.16	171.15	0.2842		

[a] Standard uncertainties (u) are $u(T)$ = 0.02 K, $u(P)$ = 0.2 kPa. The combined standard uncertainty (u_c) in density is $u_c(\rho)$ = 2 kg·m^{-3}. [b] Data taken from ref 27. (Data collected using the pyknometric method.) [c] Data taken from ref 28. (Data collected using the pyknometric method.) [d] Data taken from ref 29. (Data collected using the pyknometric method.) [e] Data taken from ref 30. (Data collected using the pyknometric method.) [f] Data taken from ref 31. (Data collected using an Anton-Paar DMA 4500 M vibrating-tube densimeter.)

concentration and density data were further used to obtain the uncertainties in the derived compressibility properties using the method of propagation of errors. All of the data of the derived thermodynamic properties with their corresponding uncertainties are tabulated below in the Results section. More details are given elsewhere.[18,21,22,26]

3. RESULTS

3.1. Thermodynamic and Volumetric Properties.

The density (ρ) and molar volume (V_m) data of pure diethylammonium-based PILs at different temperatures are reported in Table 2. It is found that the density of pure DEAF and DEAA at 298.15 K shows small discrepancies with the literature data[27−31] (see Table 2), which may be due to the difference in water content and the techniques used for the measurement of density. The density of pure DEAF at 298.15 K is reported by the same author[27,28] and has a relative density deviation of about 5%, and the present data are considered to be reasonable since the values are between them. The density of DEAA is also compared with the available literature data[29−31] in Figure 1 (also in Table 2) as a function of temperature. A density value at 293.15 K for DEAA is less than the value reported by Zhao et al.[29] using the pyknometric method with temperature control of ±2 K, and it may due to differences in the techniques used for measurement and a greater deviation in temperature control. Furthermore, Zhao et al.[29] have used the same abbreviation of DEAA for two ionic liquids, namely, diethanolammonium acetate and diethylammonium acetate, hence it is not clear to which ionic liquid the reported value with the DEAA abbreviation belongs. The density of DEAA at 298.15 K in this work is in between the densities reported by Zhu et al.[30] and Govinda et al.,[31] so it seems to be realistic. The density data of DEAA reported by Govinda et al.[31] at temperatures (298.15, 303.15, and 308.15 K) show thoroughly higher values and may be due to the lower water content (less than 70 ppm for all studied ILs) in the synthesized ILs by Govinda et al.[31] The standard entropy (S^0) from the molecular volumes (V_{molc}) of the studied PILs was calculated using eq 1 given by Glasser[32] at 298.15 K, and the results are presented in Table 2

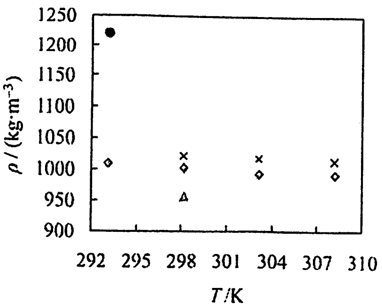

Figure 1. Experimental density (ρ) of DEAA is compared with literature data as a function of temperature (T): this work, ◆; ref 29, ●; ref 30, ▲; and ref 31, ×.

$$S^0(\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}) \approx 1246V_{molc} + 29.5 \qquad (1)$$

The lattice potential energy (U_{POT}), i.e., crystal energy, at 298.15 K for simple 1:1 inorganic salts can be calculated from eq 2[33,34]

$$U_{POT}(\mathrm{kJ{\cdot}mol^{-1}}) \approx 2I\{\alpha'(V_{molc})^{-1/3} + \beta'\} \qquad (2)$$

where α' and β' are fitting coefficients, ionic strength (I) = 1, and the molecular volume (V_{molc}) is presented in nm^3. The values of α' and β' have recently been used as 83.3 kJ·mol^{-1} nm and 153 kJ·mol^{-1}, respectively, by Gutowski.[35]

The density (ρ) data of aqueous solutions of diethylammonium-based PILs in the concentration range of (~0.02 to ~0.5) mol·kg^{-1} at different temperatures are reported in Tables 3−6. In Figure 2, the density data of aqueous solutions of DEAA as a function of the mole fraction of water (x_{water}) at 298.15 K are compared with the literature data reported by Zhu

Table 3. Molality (m), Experimental Density (ρ), Apparent Molal Volume (ϕ_V), Partial Molal Volume of Solute ($\overline{V}_2$), Solvent ($\overline{V}_1$), and Coefficient of Thermal Expansion (α) for Aqueous Solutions of DEAF at Different Temperatures (T) and at Ambient Pressure of 94.4 kPa[a]

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\overline{V}_2$/m^3·mol^{-1}	$10^6\overline{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\overline{V}_2$/m^3·mol^{-1}	$10^6\overline{V}_1$/m^3·mol^{-1}	$10^4\alpha$ /K^{-1}
T = 293.15 K						T = 298.15 K					
0.0000	998.21			18.047	2.125	0.0000	997.05			18.068	2.567
0.0187	998.28	115.58 ± 0.27	115.64 ± 0.27	18.047	2.130	0.0187	997.12	115.86 ± 0.27	115.93 ± 0.27	18.068	2.570
0.0390	998.35	115.65 ± 0.13	115.70 ± 0.13	18.047	2.133	0.0390	997.19	115.85 ± 0.13	115.91 ± 0.13	18.068	2.572
0.0589	998.42	115.63 ± 0.09	115.67 ± 0.09	18.047	2.140	0.0589	997.26	115.86 ± 0.09	115.91 ± 0.09	18.068	2.577
0.0782	998.50	115.63 ± 0.06	115.65 ± 0.06	18.047	2.139	0.0782	997.33	115.84 ± 0.06	115.87 ± 0.06	18.068	2.577
0.0980	998.57	115.62 ± 0.05	115.61 ± 0.05	18.047	2.148	0.0980	997.40	115.89 ± 0.05	115.90 ± 0.05	18.068	2.584
0.1180	998.64	115.64 ± 0.04	115.60 ± 0.04	18.047	2.148	0.1180	997.47	115.86 ± 0.04	115.85 ± 0.04	18.068	2.585
0.1310	998.69	115.63 ± 0.04	115.58 ± 0.04	18.047	2.159	0.1310	997.51	115.89 ± 0.04	115.87 ± 0.04	18.068	2.592
0.1409	998.72	115.64 ± 0.04	115.58 ± 0.04	18.047	2.155	0.1409	997.55	115.87 ± 0.04	115.84 ± 0.04	18.068	2.591
0.1626	998.81	115.62 ± 0.03	115.54 ± 0.03	18.047	2.161	0.1626	997.62	115.89 ± 0.03	115.84 ± 0.03	18.068	2.595
0.1903	998.91	115.60 ± 0.03	115.50 ± 0.03	18.047	2.173	0.1903	997.72	115.87 ± 0.03	115.80 ± 0.03	18.068	2.605
0.2254	999.03	115.61 ± 0.02	115.47 ± 0.02	18.048	2.183	0.2254	997.85	115.85 ± 0.02	115.76 ± 0.02	18.068	2.611
0.2686	999.20	115.54 ± 0.02	115.39 ± 0.02	18.048	2.213	0.2686	998.00	115.86 ± 0.02	115.76 ± 0.02	18.068	2.635
0.3188	999.38	115.55 ± 0.02	115.38 ± 0.02	18.048	2.212	0.3188	998.17	115.84 ± 0.02	115.74 ± 0.02	18.069	2.635
0.3733	999.58	115.53 ± 0.01	115.36 ± 0.01	18.048	2.241	0.3733	998.37	115.82 ± 0.01	115.73 ± 0.01	18.069	2.663
0.4103	999.72	115.50 ± 0.01	115.35 ± 0.01	18.048	2.264	0.4103	998.49	115.81 ± 0.01	115.75 ± 0.01	18.068	2.679
0.4917	1000.03	115.46 ± 0.01	115.37 ± 0.01	18.048	2.299	0.4917	998.78	115.78 ± 0.01	115.81 ± 0.01	18.068	2.715
T = 303.15 K						T = 308.15 K					
0.0000	995.65			18.093	3.010	0.0000	994.04			18.123	3.455
0.0187	995.72	116.02 ± 0.27	116.09 ± 0.27	18.093	3.011	0.0187	994.10	116.20 ± 0.27	116.29 ± 0.27	18.123	3.455
0.0390	995.79	116.08 ± 0.13	116.16 ± 0.13	18.093	3.013	0.0390	994.18	116.19 ± 0.13	116.28 ± 0.13	18.123	3.455
0.0589	995.86	116.11 ± 0.09	116.18 ± 0.09	18.093	3.015	0.0589	994.24	116.20 ± 0.09	116.38 ± 0.09	18.123	3.456
0.0782	995.93	116.07 ± 0.06	116.12 ± 0.06	18.093	3.017	0.0782	994.31	116.29 ± 0.06	116.36 ± 0.06	18.123	3.459
0.0980	996.00	116.08 ± 0.05	116.12 ± 0.05	18.093	3.021	0.0980	994.38	116.32 ± 0.05	116.39 ± 0.05	18.123	3.461
0.1180	996.06	116.10 ± 0.04	116.12 ± 0.04	18.093	3.024	0.1180	994.45	116.33 ± 0.04	116.38 ± 0.04	18.123	3.465
0.1310	996.11	116.12 ± 0.04	116.13 ± 0.04	18.093	3.027	0.1310	994.49	116.36 ± 0.04	116.41 ± 0.04	18.123	3.464
0.1409	996.14	116.09 ± 0.04	116.10 ± 0.04	18.093	3.028	0.1409	994.52	116.36 ± 0.04	116.39 ± 0.04	18.123	3.467
0.1626	996.22	116.10 ± 0.03	116.09 ± 0.04	18.093	3.031	0.1626	994.60	116.32 ± 0.03	116.34 ± 0.03	18.123	3.469
0.1903	996.31	116.12 ± 0.03	116.10 ± 0.03	18.093	3.038	0.1903	994.69	116.33 ± 0.03	116.34 ± 0.03	18.123	3.473
0.2254	996.43	116.13 ± 0.02	116.09 ± 0.02	18.093	3.041	0.2254	994.81	116.32 ± 0.02	116.32 ± 0.02	18.123	3.473
0.2686	996.57	116.13 ± 0.02	116.09 ± 0.02	18.093	3.059	0.2686	994.95	116.34 ± 0.02	116.33 ± 0.02	18.123	3.486
0.3188	996.74	116.11 ± 0.02	116.08 ± 0.02	18.093	3.059	0.3188	995.11	116.34 ± 0.02	116.33 ± 0.02	18.123	3.485
0.3733	996.92	116.12 ± 0.01	116.12 ± 0.01	18.093	3.087	0.3733	995.29	116.35 ± 0.01	116.36 ± 0.01	18.123	3.512
0.4103	997.04	116.10 ± 0.01	116.15 ± 0.01	18.093	3.096	0.4103	995.41	116.34 ± 0.01	116.38 ± 0.01	18.122	3.515
0.4917	997.31	116.09 ± 0.01	116.25 ± 0.01	18.092	3.132	0.4917	995.66	116.36 ± 0.01	116.48 ± 0.01	18.122	3.552
T = 313.15 K											
0.0000	992.22			18.156	3.903						
0.0187	992.29	116.41 ± 0.27	116.50 ± 0.27	18.156	3.901						
0.0390	992.36	116.47 ± 0.13	116.58 ± 0.13	18.156	3.900						
0.0589	992.43	116.46 ± 0.09	116.61 ± 0.09	18.156	3.898						
0.0782	992.49	116.57 ± 0.07	116.63 ± 0.07	[illegible]156	3.903						

Table 3. continued

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$ /K^{-1}
0.0980	992.56	116.53 ± 0.05	116.65 ± 0.05	18.156	3.902						
0.1180	992.63	116.54 ± 0.04	116.67 ± 0.04	18.156	3.909						
0.1310	992.67	116.55 ± 0.04	116.67 ± 0.04	18.156	3.904						
0.1409	992.70	116.54 ± 0.04	116.66 ± 0.04	18.156	3.909						
0.1626	992.77	116.62 ± 0.03	116.66 ± 0.03	18.156	3.909						
0.1903	992.86	116.62 ± 0.03	116.68 ± 0.03	18.156	3.911						
0.2254	992.98	116.60 ± 0.02	116.65 ± 0.02	18.156	3.907						
0.2686	993.10	116.67 ± 0.02	116.70 ± 0.02	18.156	3.914						
0.3188	993.26	116.68 ± 0.02	116.73 ± 0.02	18.155	3.914						
0.3733	993.42	116.69 ± 0.01	116.77 ± 0.01	18.155	3.940						
0.4103	993.55	116.66 ± 0.01	116.80 ± 0.01	18.155	3.936						
0.4917	993.78	116.70 ± 0.01	116.94 ± 0.01	18.154	3.973						

^{a}Standard uncertainties (u) are $u(T) = 0.02$ K, $u(P) = 0.2$ kPa, and $u(m) = 1 \times 10^{-4}$ mol·kg^{-1}. The combined standard uncertainties (u_c) are $u_c(\rho) = 2$ kg·m^{-3}, $u_c(\bar{V}_1) = 2 \times 10^{-9}$ m^3·mol^{-1}, and $u_c(\alpha) = 3 \times 10^{-7}$ K^{-1}.

et al.[39] and Umapathi et al.[36] The deviation between these two literature data sets is very large; their comparison with our data is very difficult since our data are for a very dilute concentration range and no single data point from the literature is available within our studied concentration range. However, the trend observed for our data is in harmony with the data reported by Umapathi et al.[36]

The apparent molal volume (ϕ_V), the partial molal volume of solvent ($\bar{V}_1$), and the partial molal volume of solute ($\bar{V}_2$) of aqueous PIL solutions were calculated from experimental density data using standard eqs 3−5.[37] The data of ϕ_V, $\bar{V}_1$, and $\bar{V}_2$ and the corresponding uncertainties are included in Tables 3−6.

$$\phi_V = \left(\frac{M_2}{\rho}\right) + \left(\frac{\rho_0 - \rho}{m\rho\rho_0}\right) \tag{3}$$

$$\bar{V}_2 = \phi_V + \frac{m^{1/2}}{2}\frac{d\phi_V}{d\sqrt{m}} \tag{4}$$

$$\bar{V}_1 = V_1^0 - \frac{M_1 m^{3/2}}{2}\frac{d\phi_V}{d\sqrt{m}} \tag{5}$$

In eqs 3−5, M_2 is the molar mass of PILs in kg·mol^{-1} and m is the molality in mol·kg^{-1}, whereas ρ_0 and ρ represent the densities in kg·m^{-3} for water and aqueous PIL solutions, respectively. V_1^0 is the molar volume of pure water, and M_1 is the molar mass of the solvent in kg·mol^{-1}. All data were obtained at temperatures of T = (293.15 to 313.15) K with a 5 K interval for aqueous solutions of PILs and are given in Tables 3−6. The ϕ_V data can be fitted with concentration (mol·kg^{-1}) using eq 6

$$\phi_V = \phi_V^0 + A_V\sqrt{m} + B_V m + D_V m^2 \tag{6}$$

where ϕ_V^0 is the limiting apparent molar volume of the studied PILs and A_V is the Debye−Hückel limiting slope. A_V values at different temperatures for aqueous solutions of 1:1 electrolyte are taken from refs 21 and 38. B_V and D_V are the deviation parameters. The quantity ($\phi_V - A_V\sqrt{m}$) was plotted against the molality (m) of the PILs, and the limiting apparent molar volume (ϕ_V^0) values were obtained by smooth extrapolation at infinite dilution as shown in Figure 3. The data of ϕ_V^0 and deviation parameters B_V and D_V are reported in Table 7. The respective uncertainties in the apparent molar volume estimated by using the method of propagation of errors are given in Tables 3−6. The apparent molar data were further used to calculate the partial molal volumes of solvent ($\bar{V}_1$) and solute ($\bar{V}_2$) by using the standard equations, and the values obtained are included in Tables 3−6. Using different temperature density data, the isobaric expansivity (α) has been calculated for the studied aqueous solutions of PILs by using eq 7.

$$\alpha = -(1/\rho)(d\rho/dT) \tag{7}$$

3.2. Acoustic Properties. The speed-of-sound data for aqueous solutions of PILs in the concentration range of (~0.05 to ~0.5) mol·kg^{-1} at 298.15 K are reported in Table 8. The experimental speed-of-sound value for pure water obtained is (1497.6 ± 0.5) m·s^{-1} at 298.15 K and is within experimental uncertainties. It is in close agreement with literature data [Gardas et al.,[18,22] 1497.6 m·s^{-1}; Wagner and Pruß,[39] 1496.7 m s^{-1} (calculated using the equation provided in the paper)

Table 4. Molality (m), Experimental Density (ρ), Apparent Molal Volume (ϕ_V), Partial Molal Volume of Solute ($\overline{V}_2$), Solvent ($\overline{V}_1$), and Coefficient of Thermal Expansion (α) for Aqueous Solutions of DEAA at Different Temperatures (T) and at Ambient Pressure of 94.5 kPa[a]

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\overline{V}_2$/m^3·mol^{-1}	$10^6\overline{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\overline{V}_2$/m^3·mol^{-1}	$10^6\overline{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}
		T = 293.15 K						T = 298.15 K			
0.0000	998.21			18.047	2.125	0.0000	997.05			18.068	2.567
0.0395	998.44	127.41 ± 0.13	127.44 ± 0.13	18.047	2.133	0.0395	997.28	127.63 ± 0.13	127.69 ± 0.13	18.068	2.572
0.0594	998.56	127.39 ± 0.08	127.39 ± 0.08	18.047	2.139	0.0594	997.39	127.67 ± 0.08	127.71 ± 0.08	18.068	2.577
0.0777	998.67	127.39 ± 0.06	127.36 ± 0.06	18.047	2.146	0.0777	997.50	127.68 ± 0.06	127.70 ± 0.06	18.068	2.581
0.0988	998.79	127.44 ± 0.05	127.37 ± 0.05	18.047	2.147	0.0988	997.62	127.70 ± 0.05	127.68 ± 0.05	18.068	2.583
0.1277	998.96	127.37 ± 0.04	127.25 ± 0.04	18.047	2.162	0.1277	997.79	127.67 ± 0.04	127.62 ± 0.04	18.068	2.594
0.1510	999.10	127.35 ± 0.03	127.18 ± 0.03	18.047	2.168	0.1510	997.92	127.66 ± 0.03	127.57 ± 0.03	18.068	2.601
0.1675	999.20	127.33 ± 0.03	127.13 ± 0.03	18.048	2.181	0.1675	998.01	127.68 ± 0.03	127.56 ± 0.03	18.068	2.611
0.1910	999.34	127.33 ± 0.03	127.09 ± 0.03	18.048	2.183	0.1910	998.15	127.62 ± 0.03	127.48 ± 0.03	18.068	2.614
0.2362	999.62	127.25 ± 0.02	126.94 ± 0.02	18.048	2.210	0.2362	998.41	127.59 ± 0.02	127.38 ± 0.02	18.069	2.635
0.2908	999.95	127.20 ± 0.02	126.81 ± 0.02	18.049	2.234	0.2908	998.74	127.53 ± 0.02	127.25 ± 0.02	18.069	2.657
0.3350	1000.22	127.14 ± 0.02	126.70 ± 0.02	18.050	2.247	0.3350	998.99	127.49 ± 0.02	127.16 ± 0.02	18.070	2.672
0.3927	1000.58	127.07 ± 0.01	126.58 ± 0.01	18.050	2.297	0.3927	999.33	127.45 ± 0.01	127.06 ± 001	18.071	2.707
0.4370	1000.85	127.03 ± 0.01	126.51 ± 0.01	18.051	2.311	0.4370	999.59	127.40 ± 0.01	126.99 ± 0.01	18.071	2.724
0.5305	1001.44	126.91 ± 0.01	126.36 ± 0.01	18.052	2.373	0.5305	1000.14	127.32 ± 0.01	126.86 ± 0.01	18.072	2.777
		T = 303.15 K						T = 308.15 K			
0.0000	995.65			18.093	3.010	0.0000	994.04			18.123	3.455
0.0395	995.88	127.88 ± 0.13	127.95 ± 0.13	18.093	3.012	0.0395	994.27	128.07 ± 0.13	128.18 ± 0.13	18.123	3.455
0.0594	995.99	127.90 ± 0.08	127.96 ± 0.08	18.093	3.015	0.0594	994.38	128.09 ± 0.09	128.20 ± 0.09	18.123	3.456
0.0777	996.10	127.90 ± 0.07	127.94 ± 0.07	18.093	3.017	0.0777	994.48	128.13 ± 0.07	128.22 ± 0.07	18.123	3.456
0.0988	996.22	127.90 ± 0.05	127.92 ± 0.05	18.093	3.020	0.0988	994.59	128.18 ± 0.05	128.26 ± 0.05	18.123	3.460
0.1277	996.38	127.89 ± 0.04	127.88 ± 0.04	18.093	3.028	0.1277	994.75	128.20 ± 0.04	128.26 ± 0.04	18.123	3.464
0.1510	996.51	127.90 ± 0.03	127.85 ± 0.03	18.093	3.035	0.1510	994.88	128.19 ± 0.03	128.22 ± 0.03	18.123	3.472
0.1675	996.60	127.91 ± 0.03	127.84 ± 0.03	18.093	3.042	0.1675	994.97	128.22 ± 0.03	128.24 ± 0.03	18.123	3.475
0.1910	996.73	127.91 ± 0.03	127.81 ± 0.03	18.094	3.047	0.1910	995.10	128.21 ± 0.03	128.20 ± 0.03	18.123	3.482
0.2362	997.00	127.85 ± 0.02	127.71 ± 0.02	18.094	3.061	0.2362	995.35	128.20 ± 0.02	128.14 ± 0.02	18.123	3.490
0.2908	997.30	127.84 ± 0.02	127.63 ± 0.02	18.094	3.081	0.2908	995.65	128.16 ± 0.02	128.05 ± 0.02	18.123	3.507
0.3350	997.55	127.80 ± 0.02	127.55 ± 0.02	18.095	3.098	0.3350	995.90	128.12 ± 0.02	127.95 ± 0.02	18.124	3.527
0.3927	997.88	127.76 ± 0.01	127.46 ± 0.01	18.095	3.118	0.3927	996.21	128.11 ± 0.01	127.88 ± 0.01	18.124	3.532
0.4370	998.13	127.73 ± 0.01	127.40 ± 0.01	18.096	3.138	0.4370	996.45	128.08 ± 0.01	127.80 ± 0.01	18.125	3.555
0.5305	998.67	127.64 ± 0.01	127.26 ± 0.01	18.097	3.182	0.5305	996.95	128.05 ± 0.01	127.66 ± 0.01	18.126	3.590
		T = 313.15 K									
0.0000	992.22			18.156	3.903						
0.0395	992.45	128.29 ± 0.13	128.42 ± 0.13	18.156	3.900						
0.0594	992.56	128.37 ± 0.09	128.50 ± 0.09	18.156	3.899						
0.0777	992.67	128.35 ± 0.07	128.48 ± 0.07	18.156	3.896						
0.0988	992.78	128.41 ± 0.05	128.53 ± 0.05	18.156	3.902						
0.1277	992.94	128.43 ± 0.04	128.53 ± 0.04	18.156	3.902						
0.1510	993.06	128.47 ± 0.03	128.56 ± 0.03	18.156	3.910						
0.1675	993.15	128.50 ± 0.03	128.57 ± 0.03	18.156	3.910						
0.1910	993.27	128.49 ± 0.03	128.55 ± 0.03	18.156	3.918						

Table 4. continued

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}
0.2362	993.52	128.47 ± 0.02	128.48 ± 0.02	18.156	3.921						
0.2908	993.81	128.47 ± 0.02	128.42 ± 0.02	18.156	3.935						
0.3350	994.04	128.48 ± 0.02	128.38 ± 0.02	18.157	3.958						
0.3927	994.36	128.42 ± 0.01	128.25 ± 0.01	18.157	3.948						
0.4370	994.59	128.43 ± 0.01	128.20 ± 0.01	18.158	3.974						
0.5305	995.08	128.38 ± 0.01	128.03 ± 0.01	18.159	3.999						

[a]Standard uncertainties (u) are $u(T)$ = 0.02 K, $u(P)$ = 0.2 kPa, and $u(m) = 1 \times 10^{-4}$ mol·kg^{-1}. The combined standard uncertainties (u_c) are $u_c(\rho)$ = 2 kg·m^{-3}, $u_c(\bar{V}_1) = 2 \times 10^{-9}$ m^3·mol^{-1}, and $u_c(\alpha) = 3 \times 10^{-7}$ K^{-1}.

Vasanthakumar et al.,[40] 1497.4 m·s^{-1}; Grande et al.,[41] 1497.12 m·s^{-1}; Wilson,[42] 1497.25 m·s^{-1}; Bilaniuk and Wong,[43] 1496.7 m·s^{-1}; and Greenspan and Tschiegg,[44] 1497.0 m·s^{-1}). Umapathi et al.[36] have reported speed-of-sound data for aqueous DEAA solutions at 298.15 K over a wide concentration range and have compared these data with the data reported in this work for said system as shown in Figure 4. The data reported in the literature are, again, at higher concentrations than those studied in this work, and it is difficult to make a direct comparison. Still, we observed a significantly large deviation from the reported literature data. The speed of sound is a very sensitive property to concentration and temperature variations. It is not clear from the experimental details provided by Umapathi et al.[36] how the mixing of water and viscous ionic liquids has been made since at higher concentrations of DEAA and other reported ionic liquids it is very difficult to form a homogeneous mixture of water and an ionic liquid under normal laboratory conditions. (For example, to prepare a mixture containing 0.5 mole fraction of water and 0.5 mole fraction of DEAA, 1 g of water has to be homogeneously mixed with 7.3934 g of DEAA, and for a higher mole fraction of DEAA, the homogeneous mixing is very difficult and is a diffusion-controlled process.) Therefore, the reliable comparison of data can be made only after getting new data for the whole concentration range along with complete experimental details on the preparation of homogeneous mixtures.

The isentropic compressibility (β_S) data of aqueous PILs solutions were obtained using Laplace equation $\beta_S = 1/(u^2\rho)$ and are included in Table 8. The β_S value estimated for pure water obtained from the experimental data is in close agreement with that reported in the literature (44.7780×10^{-8} kPa^{-1}).[45] The isothermal compressibility (β_T) for aqueous solutions of PILs was calculated using eq 8

$$\beta_T - \beta_S = \delta = \alpha^2 T/\sigma = \alpha^2 T/C_p\rho \tag{8}$$

where α is the coefficient of thermal expansion, σ is the volumetric specific heat, and δ is the difference between the isothermal and adiabatic compressibilities. The C_P value of 4.1793 J·K^{-1}·g^{-1} for the water is taken from the literature,[45] and it is assumed that the C_P value of the solvent remains constant over the studied concentration range. The obtained uncertainties in the β_S and β_T values by using the method of propagation of errors were found to be approximately $\pm 2.11 \times 10^{-10}$ kPa^{-1} and $\pm 2.13 \times 10^{-10}$ kPa^{-1}, respectively. The variations of β_S and β_T with the molality of the PILs at 298.15 K are shown in Figures 5 and 6, respectively. It is observed that isentropic compressibility (β_S) and isothermal compressibility (β_T) decrease with an increase in the molality of the PILs. The data of β_S and β_T were used to calculate the apparent molar isentropic (ϕ_{KS}) and isothermal (ϕ_{KT}) compressibilities by using eq 9

$$\phi_K = \left(\frac{M_2\beta}{\rho}\right) + \left[\frac{(\beta\rho_0 - \beta^0\rho)}{m\rho\rho_0}\right] \tag{9}$$

In eq 9, β^0 and β represent the (isentropic and isothermal) compressibilities of pure water and solution, respectively.

Figures 7 and 8 represent the concentration dependence of ϕ_{KS} and ϕ_{KT} at 298.15 K, respectively, in which it is observed that both increase with an increase in concentration. The apparent molar compressibility (ϕ_K) can be expressed as follows

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Table 5. Molality (m), Experimental Density (ρ), Apparent Molal Volume (ϕ_V), Partial Molal Volume of Solute ($\bar{V}_2$), Solvent ($\bar{V}_1$), and Coefficient of Thermal Expansion (α) for Aqueous Solutions of DEAP at Different Temperatures (T) and at Ambient Pressure of 94.5 kPa[a]

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}
		T = 293.15 K						T = 298.15 K			
0.0000	998.21			18.047	2.125	0.0000	997.05			18.068	2.567
0.0185	998.31	145.64 ± 0.27	145.70 ± 0.27	18.047	2.137	0.0185	997.16	146.11 ± 0.27	146.18 ± 0.27	18.068	2.576
0.0367	998.42	145.64 ± 0.14	145.68 ± 0.14	18.047	2.150	0.0367	997.26	146.12 ± 0.14	146.17 ± 0.14	18.068	2.587
0.0561	998.53	145.65 ± 0.09	145.65 ± 0.09	18.047	2.169	0.0561	997.35	146.12 ± 0.09	146.15 ± 0.09	18.068	2.601
0.0755	998.64	145.61 ± 0.07	145.58 ± 0.07	18.047	2.183	0.0755	997.46	146.12 ± 0.07	146.12 ± 0.07	18.068	2.613
0.0945	998.75	145.62 ± 0.05	145.55 ± 0.05	18.047	2.205	0.0945	997.56	146.09 ± 0.05	146.05 ± 0.05	18.068	2.629
0.1124	998.85	145.64 ± 0.04	145.53 ± 0.04	18.047	2.208	0.1124	997.66	146.11 ± 0.04	146.04 ± 0.04	18.068	2.635
0.1355	998.99	145.59 ± 0.04	145.43 ± 0.04	18.047	2.234	0.1355	997.78	146.10 ± 0.04	145.99 ± 0.04	18.068	2.655
0.1488	999.07	145.56 ± 0.03	145.37 ± 0.03	18.047	2.237	0.1488	997.85	146.11 ± 0.03	145.98 ± 0.03	18.068	2.661
0.1747	999.21	145.55 ± 0.03	145.31 ± 0.03	18.048	2.249	0.1747	997.99	146.08 ± 0.03	145.90 ± 0.03	18.069	2.673
0.1873	999.29	145.55 ± 0.03	145.28 ± 0.03	18.048	2.258	0.1873	998.06	146.07 ± 0.03	145.87 ± 0.03	18.069	2.681
0.2370	999.58	145.45 ± 0.02	145.08 ± 0.02	18.049	2.306	0.2370	998.34	145.99 ± 0.02	145.70 ± 0.02	18.069	2.718
0.2970	999.94	145.37 ± 0.02	144.87 ± 0.02	18.050	2.333	0.2970	998.67	145.93 ± 0.02	145.53 ± 0.02	18.070	2.750
0.3357	1000.18	145.29 ± 0.02	144.71 ± 0.02	18.050	2.411	0.3357	998.89	145.87 ± 0.02	145.41 ± 0.02	18.071	2.804
0.4034	1000.61	145.15 ± 0.01	144.45 ± 0.01	18.052	2.474	0.4034	999.28	145.79 ± 0.01	145.23 ± 0.01	18.072	2.857
0.4289	1000.77	145.12 ± 0.01	144.38 ± 0.01	18.053	2.473	0.4289	999.43	145.73 ± 0.01	145.14 ± 0.01	18.073	2.857
0.5223	1001.36	144.97 ± 0.01	144.08 ± 0.01	18.055	2.576	0.5223	999.97	145.61 ± 0.01	144.91 ± 0.01	18.075	2.950
		T = 303.15 K						T = 308.15 K			
0.0000	995.65			18.093	3.010	0.0000	994.04			18.123	3.455
0.0185	995.75	146.47 ± 0.27	146.54 ± 0.27	18.093	3.017	0.0185	994.13	147.01 ± 0.27	147.08 ± 0.27	18.123	3.460
0.0367	995.85	146.47 ± 0.14	146.53 ± 0.14	18.093	3.026	0.0367	994.22	147.10 ± 0.14	147.17 ± 0.14	18.123	3.467
0.0561	995.94	146.58 ± 0.09	146.61 ± 0.09	18.093	3.035	0.0561	994.31	147.12 ± 0.09	147.17 ± 0.09	18.123	3.472
0.0755	996.05	146.55 ± 0.07	146.56 ± 0.07	18.093	3.045	0.0755	994.41	147.09 ± 0.07	147.12 ± 0.07	18.123	3.479
0.0945	996.14	146.59 ± 0.05	146.57 ± 0.05	18.093	3.055	0.0945	994.49	147.16 ± 0.05	147.16 ± 0.05	18.123	3.483
0.1124	996.24	146.54 ± 0.05	146.50 ± 0.05	18.093	3.064	0.1124	994.58	147.16 ± 0.05	147.14 ± 0.05	18.123	3.494
0.1355	996.35	146.55 ± 0.04	146.47 ± 0.04	18.094	3.079	0.1355	994.69	147.17 ± 0.04	147.11 ± 0.04	18.123	3.505
0.1488	996.43	146.49 ± 0.03	146.38 ± 0.03	18.094	3.086	0.1488	994.75	147.13 ± 0.03	147.05 ± 0.03	18.123	3.513
0.1747	996.56	146.48 ± 0.03	146.33 ± 0.03	18.094	3.098	0.1747	994.88	147.08 ± 0.03	146.95 ± 0.03	18.123	3.525
0.1873	996.62	146.49 ± 0.03	146.32 ± 0.03	18.094	3.105	0.1873	994.94	147.08 ± 0.03	146.92 ± 0.03	18.123	3.531
.2370	996.89	146.44 ± 0.02	146.19 ± 0.02	18.094	3.132	0.2370	995.19	147.02 ± 0.02	146.77 ± 0.02	18.124	3.548
.2970	997.21	146.34 ± 0.02	146.00 ± 0.02	18.095	3.169	0.2970	995.50	146.94 ± 0.02	146.58 ± 0.02	18.125	3.590
3357	997.41	146.35 ± 0.02	145.96 ± 0.02	18.096	3.199	0.3357	995.67	146.97 ± 0.02	146.54 ± 0.02	18.125	3.597
4034	997.77	146.26 ± 0.01	145.80 ± 0.01	18.097	3.243	0.4034	996.03	146.82 ± 0.01	146.27 ± 0.01	18.127	3.630
4289	997.92	146.22 ± 0.01	145.73 ± 0.01	18.097	3.242	0.4289	996.17	146.78 ± 0.01	146.19 ± 0.01	18.127	3.630
223	998.43	146.11 ± 0.01	145.54 ± 0.01	18.099	3.325	0.5223	996.64	146.69 ± 0.01	145.94 ± 0.01	18.130	3.703
		T = 313.15 K									
000	992.22			18.156	3.903						
85	992.31	147.27 ± 0.27	147.36 ± 0.27	18.156	3.905						
67	992.40	147.36 ± 0.14	147.46 ± 0.14	18.156	3.910						
61	992.49	147.38 ± 0.09	147.47 ± 0.09	18.156	3.910						
5	992.59	147.39 ± 0.07	147.46 ± 0.07	18.156	3.914						

Table 5. continued

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}
0.0945	992.68	147.39 ± 0.05	147.45 ± 0.05	18.156	3.914						
0.1124	992.76	147.42 ± 0.05	147.46 ± 0.05	18.156	3.927						
0.1355	992.88	147.45 ± 0.04	147.46 ± 0.04	18.156	3.932						
0.1488	992.93	147.45 ± 0.03	147.45 ± 0.03	18.156	3.943						
0.1747	993.05	147.44 ± 0.03	147.40 ± 0.03	18.156	3.954						
0.1873	993.11	147.45 ± 0.03	147.39 ± 0.03	18.156	3.960						
0.2370	993.35	147.38 ± 0.02	147.24 ± 0.02	18.156	3.966						
0.2970	993.63	147.37 ± 0.02	147.14 ± 0.02	18.157	4.013						
0.3357	993.82	147.33 ± 0.02	147.04 ± 0.02	18.158	3.996						
0.4034	994.15	147.27 ± 0.01	146.88 ± 0.01	18.159	4.019						
0.4289	994.28	147.23 ± 0.01	146.80 ± 0.01	18.159	4.019						
0.5223	994.73	147.16 ± 0.01	146.59 ± 0.01	18.161	4.082						

[a] Standard uncertainties (u) are $u(T) = 0.02$ K, $u(P) = 0.2$ kPa, and $u(m) = 1 \times 10^{-4}$ mol·kg^{-1}. The combined standard uncertainties (u_c) are $u_c(\rho) = 2$ kg·m^{-3}, $u_c(\bar{V}_1) = 2 \times 10^{-9}$ m^3·mol^{-1}, and $u_c(\alpha) = 3 \times 10^{-7}$ K^{-1}.

$$\phi_K = \phi_K^0 + S_K\sqrt{m} \tag{10}$$

where ϕ_K^0 is the limiting apparent molar compressibility and S_K is the experimental limiting slope. The data for ϕ_K^0 and S_K are given in Table 9 for the studied PILs in aqueous solutions at 298.15 K.

A solution undergoing a small, isothermal volume expansion does work against the cohesive forces, which cause a change in the internal energy (U). Function $(\mathrm{d}U/\mathrm{d}V)_T$ is known as the internal pressure (P_i), which can be expressed using an equation of state

$$P_i = (\mathrm{d}U/\mathrm{d}V)_T = T(\mathrm{d}S/\mathrm{d}V)_T - P = T(\delta P/\delta T)_V - P \tag{11}$$

Using $(\delta P/\delta T)_V = (\alpha/\beta_T)$ and assuming that atmospheric pressure P is negligible, the equation of state yields

$$P_i = (\alpha/\beta_T)T \tag{12}$$

Thus, the internal pressures for studied aqueous PILs solutions were determined with the help of eq 12 by using the data of the coefficients of thermal expansion and isothermal compressibility. The hydration number (n_h) of the PILs was estimated using eq 13 given by Passynski[23] for aqueous electrolyte solutions

$$n_h = \frac{n_1}{n_2}\left(1 - \frac{\beta_S}{\beta_S^0}\right) \tag{13}$$

where n_1 is the number of moles of water, n_2 is the number of moles of solute IL, β_S is the isentropic compressibility of solution, and β_S^0 is the isentropic compressibility of pure water. The concentration-dependent hydration numbers for the studied PILs of aqueous solutions are given in Table 8.

4. DISCUSSION

4.1. Thermodynamic Properties.

The standard entropy (S^0) (see Table 2) of the PILs is very large in magnitude compared with that of normal inorganic salts[46] (e.g., $S^0_{\mathrm{NaCl}} = 72.1$ J·K^{-1}·mol^{-1}and $S^0_{\mathrm{KCl}} = 82.6$ J·K^{-1}·mol^{-1}) or even with that of high-melting organic salts, indicating that the lattice arrangements are more disordered for the studied PILs, which might be one of the reasons for the existence of such PILs in the liquid state at room temperature. This is supported more by the observed low values of the lattice potential energy (U_{POT}) (Table 2) than by those of the fused inorganic salts.[47] Furthermore, both of these thermodynamic quantities show a linear relationship with the alkyl chain length variation of the anion, where it is observed that S^0 increases and U_{POT} decreases, respectively, with an increase in the alkyl chain length of the anion, implying that increased hydrophobicity on the anion may lower the melting temperature of the PILs.

4.2. Volumetric Properties.

The volumetric studies of aqueous solutions are essential to recognizing the structural changes of solvent due to the presence of PILs.[48,49] The apparent molal volumes (ϕ_V) decrease with an increase in the concentration of PILs, which shows analogous behavior observed for aqueous solutions of n-alkyl amines and tetraalkylammonium salts.[50,51] The plot of $\phi_V - A_V\sqrt{m}$ against molality (m) in Figure 3 shows a negative deviation from the Debye–Huckel limiting law, which is evident from the deviation parameter (B_V) for all of the studied PILs. The magnitude and sign of B_V have led to significant conclusions about ion–ion interactions at different temperatures.[50−53] The

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Table 6. Molality (m), Experimental Density (ρ), Apparent Molal Volume (ϕ_V), Partial Molal Volume of Solute ($\bar{V}_2$), Solvent ($\bar{V}_1$) and Coefficient of Thermal Expansion (α) for Aqueous Solutions of DEAB at Different Temperatures (T) and at Ambient Pressure of 94.4 kPa[a]

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}
		T = 293.15 K						T = 298.15 K			
0.0000	998.21			18.047	2.125	0.0000	997.05			18.068	2.567
0.0175	998.27	157.80 ± 0.29	157.85 ± 0.29	18.047	2.135	0.0175	997.11	158.30 ± 0.29	158.36 ± 0.29	18.068	2.575
0.0360	998.34	157.80 ± 0.14	157.83 ± 0.14	18.047	2.149	0.0360	997.17	158.38 ± 0.14	158.42 ± 0.14	18.068	2.585
0.0541	998.40	157.82 ± 0.09	157.82 ± 0.09	18.047	2.161	0.0541	997.23	158.32 ± 0.09	158.34 ± 0.09	18.068	2.597
0.0716	998.47	157.83 ± 0.07	157.80 ± 0.07	18.047	2.177	0.0716	997.29	158.34 ± 0.07	158.33 ± 0.07	18.068	2.609
0.0912	998.54	157.83 ± 0.06	157.75 ± 0.06	18.047	2.193	0.0912	997.35	158.39 ± 0.06	158.35 ± 0.06	18.068	2.622
0.1116	998.61	157.82 ± 0.05	157.69 ± 0.05	18.047	2.210	0.1116	997.42	158.34 ± 0.05	158.25 ± 0.05	18.068	2.638
0.1320	998.69	157.79 ± 0.04	157.61 ± 0.04	18.047	2.224	0.1320	997.48	158.39 ± 0.04	158.26 ± 0.04	18.068	2.652
0.1509	998.76	157.77 ± 0.03	157.54 ± 0.03	18.048	2.244	0.1509	997.54	158.35 ± 0.03	158.18 ± 0.03	18.068	2.668
0.1739	998.85	157.73 ± 0.03	157.44 ± 0.03	18.048	2.254	0.1739	997.62	158.32 ± 0.03	158.08 ± 0.03	18.069	2.681
0.1886	998.91	157.69 ± 0.03	157.36 ± 0.03	18.048	2.276	0.1886	997.68	158.28 ± 0.03	158.01 ± 0.03	18.069	2.698
0.2385	999.11	157.58 ± 0.02	157.11 ± 0.02	18.049	2.309	0.2385	997.86	158.17 ± 0.02	157.77 ± 0.02	18.070	2.733
0.2842	999.31	157.47 ± 0.02	156.86 ± 0.02	18.050	2.362	0.2842	998.03	158.09 ± 0.02	157.57 ± 0.02	18.071	2.777
0.3390	999.55	157.34 ± 0.02	156.56 ± 0.02	18.052	2.422	0.3390	998.24	157.99 ± 0.02	157.32 ± 0.02	18.072	2.831
0.3879	999.77	157.24 ± 0.01	156.32 ± 0.01	18.053	2.462	0.3879	998.45	157.86 ± 0.01	157.05 ± 0.01	18.074	2.872
0.4378	1000.01	157.13 ± 0.01	156.05 ± 0.01	18.055	2.527	0.4378	998.65	157.79 ± 0.01	156.84 ± 0.01	18.075	2.928
0.5105	1000.35	156.98 ± 0.01	155.68 ± 0.01	18.059	2.606	0.5105	998.95	157.67 ± 0.01	156.50 ± 0.01	18.079	3.005
		T = 303.15 K						T = 308.15 K			
0.0000	995.65			18.093	3.010	0.0000	994.04			18.123	3.455
0.0175	995.71	158.68 ± 0.29	158.76 ± 0.29	18.093	3.017	0.0175	994.09	159.10 ± 0.29	159.19 ± 0.29	18.123	3.460
0.0360	995.76	158.75 ± 0.14	158.83 ± 0.14	18.093	3.024	0.0360	994.14	159.25 ± 0.14	159.35 ± 0.14	18.123	3.464
0.0541	995.82	158.75 ± 0.09	158.82 ± 0.09	18.093	3.034	0.0541	994.19	159.27 ± 0.09	159.37 ± 0.09	18.123	3.474
0.0716	995.87	158.80 ± 0.07	158.84 ± 0.07	18.093	3.044	0.0716	994.23	159.33 ± 0.07	159.42 ± 0.07	18.123	3.480
0.0912	995.93	158.83 ± 0.06	158.85 ± 0.06	18.093	3.053	0.0912	994.29	159.34 ± 0.06	159.41 ± 0.06	18.123	3.486
0.1116	995.98	158.87 ± 0.05	158.86 ± 0.05	18.093	3.069	0.1116	994.34	159.39 ± 0.05	159.43 ± 0.05	18.123	3.501
0.1320	996.05	158.85 ± 0.04	158.80 ± 0.04	18.093	3.081	0.1320	994.40	159.37 ± 0.04	159.38 ± 0.04	18.123	3.513
0.1509	996.10	158.86 ± 0.03	158.78 ± 0.03	18.094	3.093	0.1509	994.45	159.37 ± 0.03	159.35 ± 0.03	18.123	3.520
0.1739	996.18	158.79 ± 0.03	158.66 ± 0.03	18.094	3.109	0.1739	994.51	159.36 ± 0.03	159.31 ± 0.03	18.123	3.540
0.1886	996.22	158.79 ± 0.03	158.63 ± 0.03	18.094	3.122	0.1886	994.55	159.38 ± 0.03	159.29 ± 0.03	18.123	3.548
0.2385	996.39	158.71 ± 0.02	158.44 ± 0.02	18.094	3.159	0.2385	994.70	159.28 ± 0.02	159.09 ± 0.02	18.124	3.588
0.2842	996.54	158.65 ± 0.02	158.26 ± 0.02	18.095	3.193	0.2842	994.84	159.23 ± 0.02	158.93 ± 0.02	18.124	3.612
0.3390	996.73	158.56 ± 0.02	158.03 ± 0.02	18.097	3.242	0.3390	995.00	159.17 ± 0.02	158.73 ± 0.02	18.125	3.655
0.3879	996.90	158.50 ± 0.01	157.83 ± 0.01	18.098	3.283	0.3879	995.17	159.08 ± 0.01	158.50 ± 0.01	18.127	3.697
0.4378	997.09	158.41 ± 0.01	157.60 ± 0.01	18.100	3.331	0.4378	995.32	159.04 ± 0.01	158.31 ± 0.01	18.128	3.736
0.5105	997.35	158.32 ± 0.01	157.28 ± 0.01	18.103	3.405	0.5105	995.55	158.97 ± 0.01	157.99 ± 0.01	18.132	3.808
		T = 313.15 K									
0.0000	992.22			18.156	3.903						
0.0175	992.27	159.55 ± 0.29	159.66 ± 0.29	18.156	3.906						
0.0360	992.32	159.61 ± 0.14	159.74 ± 0.14	18.156	3.907						
0.0541	992.36	159.77 ± 0.09	159.91 ± 0.09	18.156	3.916						
0.0716	992.41	159.74 ± 0.07	159.88 ± 0.07	18.156	3.918						

Table 6. continued

m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}	m/mol·kg^{-1}	ρ/kg·m^{-3}	$10^6\phi_V$/m^3·mol^{-1}	$10^6\bar{V}_2$/m^3·mol^{-1}	$10^6\bar{V}_1$/m^3·mol^{-1}	$10^4\alpha$/K^{-1}
0.0912	992.47	159.82 ± 0.06	159.94 ± 0.06	18.156	3.922						
0.1116	992.51	159.83 ± 0.05	159.94 ± 0.05	18.156	3.935						
0.1320	992.55	159.88 ± 0.04	159.97 ± 0.04	18.156	3.947						
0.1509	992.60	159.87 ± 0.03	159.94 ± 0.03	18.156	3.950						
0.1739	992.66	159.87 ± 0.03	159.91 ± 0.03	18.156	3.973						
0.1886	992.70	159.87 ± 0.03	159.88 ± 0.03	18.156	3.976						
0.2385	992.82	159.85 ± 0.02	159.78 ± 0.02	18.156	4.018						
0.2842	992.95	159.79 ± 0.02	159.61 ± 0.02	18.157	4.032						
0.3390	993.09	159.75 ± 0.02	159.45 ± 0.02	18.158	4.070						
0.3879	993.23	159.70 ± 0.01	159.27 ± 0.01	18.159	4.113						
0.4378	993.37	159.66 ± 0.01	159.08 ± 0.01	18.161	4.143						
0.5105	993.57	159.61 ± 0.01	158.79 ± 0.01	18.163	4.213						

[a] Standard uncertainties (u) are $u(T) = 0.02$ K, $u(P) = 0.2$ kPa, and $u(m) = 1 \times 10^{-4}$ mol·kg^{-1}. The combined standard uncertainties (u_c) are $u_c(\rho) = 2$ kg·m^{-3}, $u_c(\bar{V}_1) = 2 \times 10^{-9}$ m^3·mol^{-1}, and $u_c(\alpha) = 3 \times 10^{-7}$ K^{-1}.

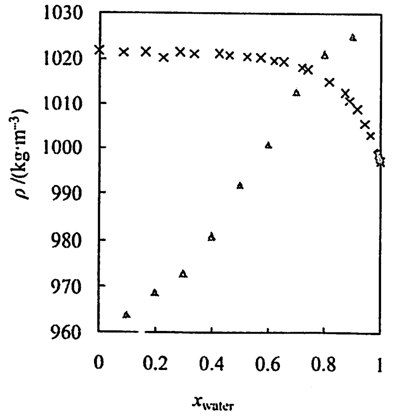

Figure 2. Experimental density (ρ) of aqueous solutions of DEAA compared with literature data as a function of the mole fraction of water (x_{water}) at 298.15 K: this work, ⧫; ref 30, ▲; and ref 36, ×.

negative B_V values for PILs in aqueous solutions indicate the favorable ion–ion interactions along with the water-structure-making effect. The B_V values become more negative with an increase in alkyl chain length, which is due to the increased hydrophobicity of the PILs. B_V values increase (become less negative) with increasing temperature, indicating the increased hydrophobic hydration as compared to the hydrophobic ion association in aqueous solutions of PILs, which is analogous to the effect observed earlier for imidazolium-based ionic liquids.[21] From Figure 9 it is observed that the ϕ_V^0 values increase with increases in the temperature and alkyl chain length of the anions of the PILs, which enhances the ion–solvent interactions, and this phenomenon was also observed in our recent studies of the triethylammonium-based carboxylate PILs[17] and 1-n-alkyl-3-methylimidazolium-based amino acid ionic liquids.[19,21]

All of these are reflected more clearly in the concentration-dependent behavior of the partial molal volume data of PILs ($\bar{V}_2$) (Tables 3–6). The partial molal volume of solvent ($\bar{V}_1$) increases slightly from the value of the molar volume of pure water with an increase in the PIL concentration as well as with an increase in the alkyl chain length of the anion, which highlights the strengthening of the water structure around the ion due to hydrophobic hydration.[54,55] This is supported by the negative values of excess molar volume V_m^E (estimated using $V_m^E = \bar{V}_2^0 - V_m$)[17,21] for the studied PILs (Table 7), which become more negative with an increase in the alkyl chain length on the anions as well as with an increase in temperature. Such behavior is also observed for many hydrophobic solutes or ions where hydrophobic hydration effects become more important than hydrophobic association at higher temperatures.

4.3. Electrostriction. The ion–solvent interactions in aqueous solutions can be better understood through electrostriction effects from which firmly bound water molecules in the primary hydration shell of ions can be estimated.[56] The negative volume change as a result of electrostriction due to ions (V_{Ele}^0) can be obtained using the expression $V_{Ele}^0 = V_{Int}^0 - \bar{V}_{ion}^0$, where V_{Int}^0 and $\bar{V}_{ion}^0$ are the intrinsic volume and the limiting partial molar volume of ions, respectively. As shown earlier[21] in studying the electrostriction of ions in ionic liquids, instead of using the crystallographic radii to estimate intrinsic volumes, it is more convenient to use the molar volumes of ionic liquids if the density data of the pure ionic liquids are available; furthermore, the molar volume can be decomposed

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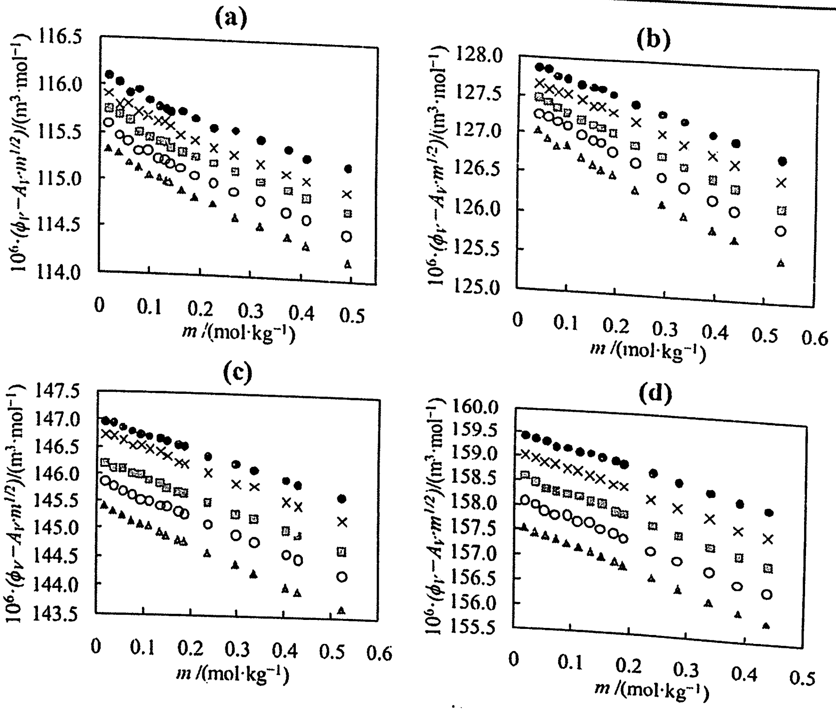

Figure 3. Variation of the parameter ($\phi_V - A_V m^{1/2}$) as a function of the molality (m) of protic ionic liquids (a) DEAF, (b) DEAA, (c) DEAP, and (d) DEAB at different temperatures: T = 293.15 K, ▲; T = 298.15 K, ○; T = 303.15 K, ■; T = 308.15 K, ×; and T = 313.15 K, ●.

Table 7. Limiting Partial Molar Volume ($\overline{V}_2^0 = \phi_V^0$), Deviation Parameter ($B_V$ and D_V), Excess Molar Volume (V_m^E), and Electrostricted Hydration Number (n_h^{ele}) Data for PILs over Temperature Range T = (293.15 to 313.15) K and at Ambient Pressure of 94.4 kPa[a]

T/K	$10^6\overline{V}_2^0$/m³·mol⁻¹	10^6B_V/m³·kg·mol⁻³	10^6D_V/m³·kg²·mol⁻³	$10^6V_m^E$/m³·mol⁻¹	n_h^{ele}
			DEAF		
293.15	115.35 ± 0.02	−2.99 ± 0.14	1.33 ± 0.22	−0.09 ± 0.02	0.03
298.15	115.55 ± 0.01	−2.78 ± 0.09	1.19 ± 0.13	−1.24 ± 0.01	0.34
303.15	115.71 ± 0.02	−2.53 ± 0.11	1.04 ± 0.17	−1.61 ± 0.02	0.46
308.15	115.95 ± 0.02	−2.49 ± 0.12	1.82 ± 0.19	−1.88 ± 0.02	0.56
313.15	116.06 ± 0.04	−2.21 ± 0.24	0.85 ± 0.38	−2.28 ± 0.04	0.72
			DEAA		
293.15	127.15 ± 0.02	−3.68 ± 0.12	1.23 ± 0.17	−4.86 ± 0.02	1.25
298.15	127.43 ± 0.01	−3.48 ± 0.09	1.34 ± 0.12	−5.39 ± 0.01	1.47
303.15	127.56 ± 0.02	−2.85 ± 0.10	0.59 ± 0.14	−6.52 ± 0.02	1.87
308.15	127.83 ± 0.02	−2.57 ± 0.14	1.06 ± 0.20	−6.74 ± 0.02	2.02
313.15	127.99 ± 0.03	−2.44 ± 0.16	0.42 ± 0.22	−7.05 ± 0.03	2.22
			DEAP		
293.15	145.45 ± 0.02	−3.91 ± 0.14	0.96 ± 0.20	−7.91 ± 0.02	2.03
298.15	145.87 ± 0.02	−3.47 ± 0.10	0.71 ± 0.14	−8.48 ± 0.02	2.30
303.15	146.26 ± 0.03	−3.45 ± 0.18	0.95 ± 0.26	−9.59 ± 0.03	2.75
308.15	146.86 ± 0.04	−3.36 ± 0.28	1.10 ± 0.40	−9.58 ± 0.04	2.88
313.15	147.07 ± 0.02	−3.21 ± 0.21	0.75 ± 0.21	−9.97 ± 0.02	3.14
			DEAB		
293.15	157.73 ± 0.02	−4.64 ± 0.13	1.29 ± 0.20	−9.35 ± 0.02	2.40
298.15	158.24 ± 0.03	−4.44 ± 0.21	1.35 ± 0.31	−9.95 ± 0.03	2.70
303.15	158.66 ± 0.02	−4.07 ± 0.15	1.28 ± 0.22	−11.16 ± 0.02	3.20
308.15	159.15 ± 0.03	−3.95 ± 0.20	1.41 ± 0.29	−11.34 ± 0.03	3.41
313.15	159.53 ± 0.02	−3.35 ± 0.16	0.98 ± 0.23	−11.62 ± 0.02	3.65

[a] Standard uncertainties (u) are $u(T)$ = 0.02 K and $u(P)$ = 0.2 kPa.

into the respective ionic contributions through Padova's approach by the anhydrous nature of the iodide ion. Accordingly, the molar volumes of ions at 298.15 K are estimated using the molar volume of an acetate ion as 46.7 × 10^{-6} m³·mol⁻¹ at 298.15 K obtained from the molar volume of the 1-*n*-butyl-3-methylimidazolium cation (Bmim$^+$)[21] and the literature density data[57] of 1-*n*-butyl-3-methylimidazolium acetate [Bmim][Ace], assuming the additivity of ionic volumes.

Table 8. Molality (m), Speed of Sound (w), Isentropic (β_S) and Isothermal (β_T) Compressibilities, Apparent Molal Isentropic (ϕ_{KS}) and Isothermal (ϕ_{KT}) Compressibilities, Internal Pressure (P_i), and Hydration Number (n_h) Data for Aqueous Solutions of PILs at 298.15 K and at Ambient Pressure of 94.4 kPa[a]

m/mol·kg^{-1}	W/m·s^{-1}	$10^8\beta_S$/kPa^{-1}	$10^8\beta_T$/kPa^{-1}	$10^{12}\phi_{KS}$/m^3·mol^{-1}·kPa^{-1}	$10^{12}\phi_{KT}$/m^3·mol^{-1}·kPa^{-1}	$10^{-2}P_i$/kPa	n_h
				DEAF			
0.0000	1497.7	44.71	45.18			1694	
0.0524	1503.2	44.38	44.85	−12.7 ± 5.7	−11.6 ± 5.7	1711	7.94
0.1016	1508.0	44.09	44.57	−10.6 ± 2.9	−9.4 ± 2.9	1728	7.63
0.1515	1512.8	43.80	44.28	−9.6 ± 1.9	−8.4 ± 2.0	1747	7.47
0.2047	1517.6	43.52	44.00	−8.2 ± 1.4	−6.9 ± 1.4	1767	7.26
0.2547	1522.0	43.26	43.75	−7.2 ± 1.1	−5.9 ± 1.2	1787	7.09
0.2993	1526.2	43.01	43.51	−7.1 ± 1.0	−5.7 ± 1.0	1806	7.05
0.3571	1531.4	42.71	43.22	−6.7 ± 0.8	−5.2 ± 0.8	1833	6.95
0.4014	1534.8	42.52	43.03	−5.6 ± 0.7	−4.1 ± 0.7	1853	6.79
0.4526	1539.2	42.27	42.79	−5.3 ± 0.6	−3.6 ± 0.6	1879	6.71
0.5307	1545.2	41.93	42.46	−4.1 ± 0.5	−2.3 ± 0.5	1919	6.52
				DEAA			
0.0000	1497.6	44.72	45.19			1691	
0.0502	1503.8	44.34	44.81	−19.5 ± 5.9	−18.1 ± 6.0	1713	9.42
0.1010	1509.8	43.97	44.45	−17.9 ± 2.9	−16.4 ± 2.9	1736	9.16
0.1491	1515.2	43.65	44.13	−16.3 ± 2.0	−14.7 ± 2.0	1758	8.91
0.2005	1521.0	43.30	43.79	−15.6 ± 1.5	−13.9 ± 1.5	1783	8.77
0.2498	1526.2	43.00	43.49	−14.3 ± 1.2	−12.5 ± 1.2	1808	8.56
0.3014	1531.4	42.69	43.20	−13.0 ± 1.0	−11.2 ± 1.0	1835	8.35
0.3490	1536.5	42.40	42.91	−12.7 ± 0.8	−10.8 ± 0.8	1863	8.26
0.4008	1541.6	42.10	42.63	−11.8 ± 0.7	−9.8 ± 0.7	1893	8.10
0.4448	1546.2	41.84	42.37	−11.5 ± 0.6	−9.5 ± 0.6	1920	8.03
0.5109	1552.4	41.49	42.04	−10.5 ± 0.6	−8.3 ± 0.6	1962	7.84
				DEAP			
0.0000	1497.6	44.72	45.19			1694	
0.0509	1505.2	44.26	44.74	−26.4 ± 5.8	−23.6 ± 5.9	1731	11.28
0.1006	1511.8	43.86	44.35	−21.6 ± 2.9	−18.7 ± 3.0	1766	10.61
0.1513	1518.4	43.47	43.97	−19.5 ± 1.9	−16.5 ± 2.0	1804	10.28
0.2032	1525.0	43.08	43.60	−18.1 ± 1.4	−14.9 ± 1.5	1843	10.02
0.2509	1530.6	42.75	43.29	−16.2 ± 1.2	−13.0 ± 1.2	1880	9.73
0.3022	1537.2	42.37	42.92	−16.0 ± 1.0	−12.7 ± 1.0	1922	9.63
0.3496	1542.8	42.06	42.62	−15.1 ± 0.8	−11.7 ± 0.8	1961	9.46
0.4007	1549.0	41.71	42.29	−14.6 ± 0.7	−11.1 ± 0.7	2006	9.33
0.4515	1555.0	41.37	41.97	−14.0 ± 0.6	−10.4 ± 0.6	2051	9.20
0.4892	1559.6	41.12	41.73	−13.9 ± 0.6	−10.2 ± 0.6	2086	9.13
				DEAB			
0.0000	1497.6	44.72	45.19			1692	
0.0518	1505.9	44.22	44.70	−26.5 ± 5.7	−23.5 ± 5.8	1732	11.96
0.1018	1513.2	43.79	44.28	−22.4 ± 2.9	−19.3 ± 2.9	1771	11.36
0.1516	1520.4	43.37	43.87	−20.9 ± 1.9	−17.5 ± 2.0	1812	11.08
0.2004	1527.2	42.97	43.50	−19.4 ± 1.5	−15.9 ± 1.5	1854	10.81
0.2526	1534.0	42.58	43.12	−17.4 ± 1.1	−13.8 ± 1.2	1900	10.49
0.2992	1540.6	42.21	42.77	−17.3 ± 1.0	−13.5 ± 1.0	1945	10.40
0.3446	1546.4	41.89	42.46	−16.2 ± 0.8	−12.3 ± 0.8	1989	10.19
0.4031	1554.2	41.46	42.06	−15.6 ± 0.7	−11.5 ± 0.7	2049	10.03
0.4507	1560.6	41.11	41.73	−15.4 ± 0.6	−11.1 ± 0.6	2100	9.93
0.5100	1568.6	40.68	41.33	−15.2 ± 0.6	−10.8 ± 0.6	2168	9.82

[a] Standard uncertainties (u) are $u(T) = 0.02$ K, $u(P) = 0.2$ kPa, and $u(m) = 1 \times 10^{-4}$ mol·kg^{-1}. The combined standard uncertainties (u_c) are $u_c(w) = 0.5$ m·s^{-1}, $u_c(\beta_S) = 2.11 \times 10^{-10}$ kPa^{-1}, $u_c(\beta_T) = 2.13 \times 10^{-10}$ kPa^{-1}, $u_c(P_i) = 2.1 \times 10^2$ kPa, and $u_c(n_h) = 0.02$.

Furthermore, the partial molar volumes of the PILs were split into ionic contributions for which the partial molar volume of the diethylammonium cation in aqueous solutions at infinite dilution was taken as 83.5×10^{-6} m^3·mol^{-1} at 298.15 K from the literature,[58] and anionic contributions were obtained by subtracting the cationic contribution from the partial molar volume PILs at 298.15 K. Thus, the estimated ionic partial molar volumes and, assuming the intrinsic volume of ions is equal to the molar volume of ions in the pure state (since the "caged" and "disordered" effects [illegible] negligibly small), the volume change due to electrostriction at infinite dilution V^0_{Ele} (electrostriction due to cations and anions are denoted by V^+_{Ele} and V^-_{Ele}, respectively) in aqueous solutions of PILs were

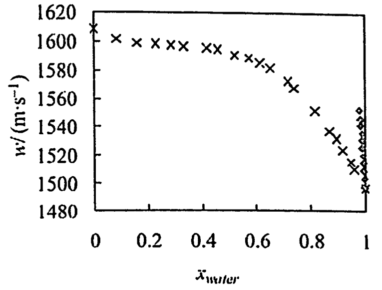

Figure 4. Experimental speed of sound (w) of aqueous solutions of DEAA is compared with the literature data as a function of the mole fraction of water (x_{water}) at 298.15 K: this work, ◆; ref 36, ×.

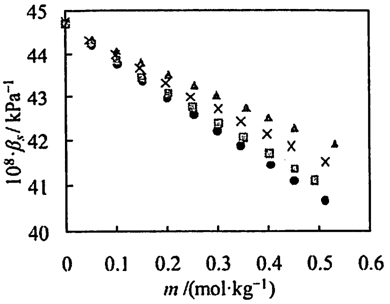

Figure 5. Variation of isentropic compressibility (β_S) as a function of the molality (m) of PILs at 298.15 K: [DEAF], ▲; [DEAA], ×; [DEAP], ■; and [DEAB], ●.

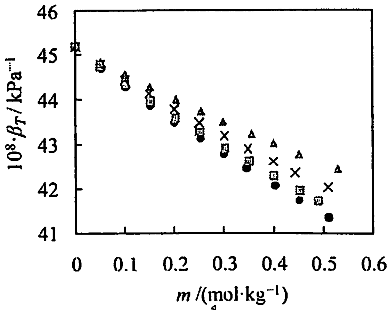

Figure 6. Variation of isothermal compressibility (β_T) as a function of the molality (m) of PILs at 298.15 K: [DEAF], ▲; [DEAA], ×; [DEAP], ■; and [DEAB], ●.

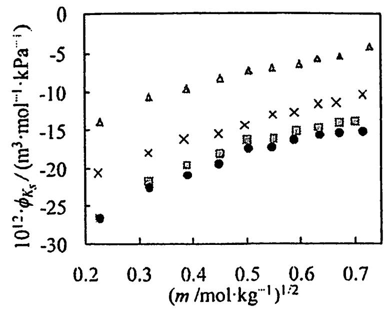

Figure 7. Dependence of the apparent molar isentropic compressibility (ϕ_{KS}) as a function of the square root molality ($m^{1/2}$) of PILs at T = 298.15 K: [DEAF], ▲; [DEAA], ×; [DEAP], ■; and [DEAB], ●.

estimated and further utilized to obtain the electrostricted hydration numbers of ions (n_h^{ion}) using eq 14

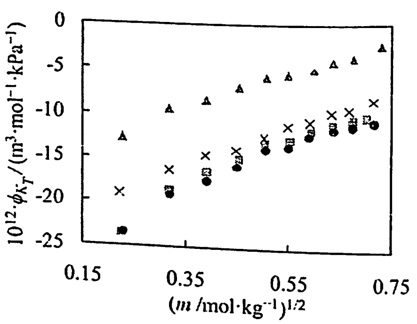

Figure 8. Dependence of the apparent molar isothermal compressibility (ϕ_{KT}) as a function of the square root molality ($m^{1/2}$) of PILs at 298.15 K: [DEAF], ▲; [DEAA], ×; [DEAP], ■; and [DEAB], ●.

$$n_h^{ion} = \frac{V_{Ele}^0}{V_{Ele}(H_2O)} \tag{14}$$

The electrostriction data for pure water [$V_{Ele}(H_2O)$] at different temperatures were taken from our earlier work.[21] The data for n_h^{ion} (n_h^+ for cations and n_h^- for anions) along with molar and partial molar volumes of ions at 298.15 K are reported in Table 10. From this data, it is found that the hydration number increases linearly with an increase in alkyl chain length on an anion, indicating the existence of hydrophobic hydration, which leads to the strengthening of the water structure around hydrophobic ions. Comparing the hydration number of the cation and different anions, it was observed that the anions have a higher share than the cation due to the strong H-bonding ability of the carboxylate functional group of the anion.

To understand the effect of temperature on the ionic hydration due to electrostriction, it is necessary to have information on individual ionic contributions to the molar volume and partial molar volume at each temperature studied. As the individual ionic volume data given in Table 10 are available only at 298.15 K, the calculations for ionic hydration due to electrostriction were made only at 298.15 K for the studied PILs. However, it is proven that the overall electrostriction for a given electrolyte is equal to the sum of the contributions from individual cations and anions at infinite dilution,[21] which leads to the additivity of hydration numbers estimated using the electrostriction approach. Accordingly, the volume change due to the electrostriction effect of ions of PILs is nothing but an excess molar volume (V_m^E) of PILs assuming the caged and disordered effects are negligibly small and are the sum of the electrostricted volume change due to the corresponding cation (V_{Ele}^+) and anion (V_{Ele}^-). The overall hydration number (having a sum of contributions from both the cation and anion) due to electrostriction (n_h^{ele}) is related to V_m^E as given in eq 15

$$n_h^{Ele} = \frac{V_m^E}{V_{Ele}(H_2O)} \tag{15}$$

Thus, the electrostricted hydration numbers for ionic liquids can be obtained using density data even though the ionic volume data are not available at different temperatures. The electrostricted hydration numbers for the studied PILs in aqueous solutions at different temperatures were estimated using eq 15 and are included in Table 7 along with the excess molar volume data. It is interesting that the electrostricted hydration numbers for the studied PILs increase not only with

Table 9. Limiting Apparent Molar Compressibility (ϕ^0_{KS} and ϕ^0_{KT}), Experimental Limiting Slope (S_{KS} and S_{KT}), and Hydration Number at Infinite Dilution (n^0_h) for Aqueous Solutions of PILs at 298.15 K and Ambient Pressure of 94.4 kPa[a]

PILs	$10^{12}\phi^0_{KS}$/m^3·mol^{-1}·kPa^{-1}	$10^{12}S_{KS}$/m^3·mol$^{-3/2}$·kg$^{-1/2}$·kPa^{-1}	$10^{12}\phi^0_{KT}$/m^3·mol^{-1}·kPa^{-1}	$10^{12}S_{KT}$/m^3·mol$^{-3/2}$·kg$^{-1/2}$·kPa^{-1}	n^0_h
DEAF	−15.8 ± 2.1	16.9 ± 7.2	−14.8 ± 2.1	16.5 ± 7.2	8.0 ± 0.09
DEAA	−25.9 ± 1.8	27.6 ± 6.5	−24.5 ± 1.8	27.1 ± 6.5	9.7 ± 0.07
DEAP	−36.5 ± 1.9	57.7 ± 7.1	−33.7 ± 2.0	57.1 ± 7.1	11.4 ± 0.11
DEAB	−38.6 ± 1.9	62.1 ± 6.9	−35.5 ± 1.9	60.8 ± 6.8	12.2 ± 0.08

[a] Standard uncertainties are $u(T)$ = 0.02 K and $u(P)$ = 0.2 kPa.

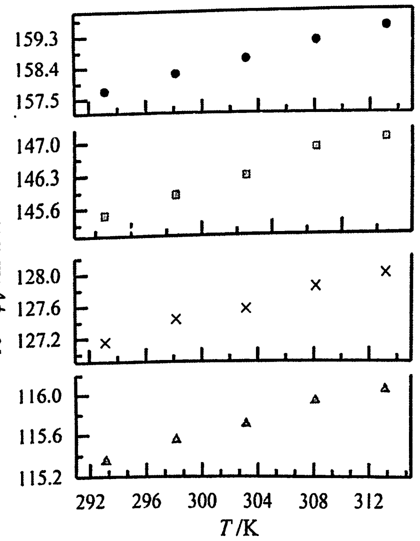

Figure 9. Limiting partial molal volume ($\phi^0_V = \bar{V}^0_2$) as a function of the temperature (T) of protic ionic liquids: DEAF, ▲; DEAA, ×; DEAP, ■; and DEAB, ●.

an increase in alkyl chain length on anions but also with an increase in temperature, providing strong evidence for the existence of hydrophobic hydration in aqueous solutions of these studied PILs, supporting an inference drawn from V^E_m data. Electrostricted hydration numbers of PILs are comparatively small due to the reduced charge density of ions in contrast to those observed for metal ions and hence exclude the dynamic water bound to the ions of PILs. However, the thermodynamically stable water of hydration can be obtained using the compressibility data, which also take into consideration the time-average number of dynamic water molecules in the hydration shell of the ions of PILs, which have been discussed herewith later.

4.4. Acoustic Properties.

The isentropic or isothermal compressibility, which is calculated from speed-of-sound data, gives evidence directly related to the changes in solvation, H-bonding, and water structure changes in the aqueous medium.[17,21,22] The order observed for a decrease in both adiabatic compressibility (β_S) and isothermal compressibility (β_T) with respect to concentration (Figures 5 and 6) for the studied PILs is [DEAF] > [DEAA] > [DEAP] > [DEAB]. The decrease in compressibility to a greater extent is due to the electrostriction of water in solution, which increases with an increase in the hydrocarbon part of the anion. The negative values of compressibility for the aqueous solutions of PILs imply that the bound water around the solute has a greater resistance to compression than does the bulk water. The ϕK_S and ϕK_T data plotted against the square root of molality ($m^{1/2}$) (Figures 7 and 8) exhibit linear behavior with positive slopes (SK_S and SK_T, respectively) (Table 9), indicating the ordering of water molecules around the solute, i.e., a water-structure-making effect. The negative values of the limiting apparent molar compressibility (ϕ^0_K) data imply that the hydrated ionic liquids are less compressible than pure water, which is due to the well-organized strong H-bonding within the hydration shell of the ions resisting the compression effects and hence the compressibility loss. Furthermore, the ϕ^0_K values become more negative with the increased hydrophobicity of the anions of PILs (Table 9), revealing the hydrophobic hydration which adds a greater compressibility loss, supporting the findings drawn from the electrostriction effects. These large compressibility losses must lead to an increase in the cohesive energy density, as is observed through the estimation of the internal pressure of aqueous solutions of PILs at 298.15 K (Table 8 and Figure 10), which increases with concentration and shows a

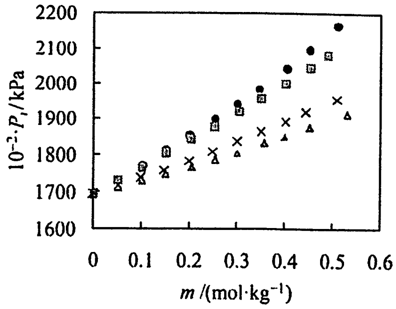

Figure 10. Dependence of internal pressure (P_i) as a function of the molality (m) of PILs at 298.15 K: [DEAF], ▲; [DEAA], ×; [DEAP], ■; and [DEAB], ●.

Table 10. Molar Volumes of Cations (V_+) and Anions (V_-), Partial Molar Volumes of Cations ($\bar{V}^0_+$) and Anions ($\bar{V}^0_-$), Electrostricted Volumes Due to Cations (V^+_{Ele}) and Anions (V^-_{Ele}), and Ionic Hydration Numbers (n^{ion}_h) for PILs in Aqueous Solutions at 298.15 K

PILs	10^6V_+/m^3·mol^{-1}	10^6V_-/m^3·mol^{-1}	$10^6\bar{V}^0_+$/m^3·mol^{-1}	$10^6\bar{V}^0_-$/m^3·mol^{-1}	$10^6V^+_{\mathrm{Ele}}$/m^3·mol^{-1}	$10^6V^-_{\mathrm{Ele}}$/m^3·mol^{-1}	n^+_h	n^-_h
DEAF	86.2	30.6	83.5	32.0	−2.6	−1.4	0.72	0.38
DEAA	86.2	46.7	83.5	43.9	−2.6	−2.7	0.72	0.75
DEAP	86.2	68.1	83.5	62.3	−2.6	−5.8	0.72	1.59
DEAB	86.2	82.0	83.5	74.7	−2.6	−7.3	0.72	1.99

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more enhanced effect when the hydrophobicity of the anions of the studied PILs increases. The overall combined outcome of all of the above findings must lead to large hydration numbers for PILs, which must increase with the increased hydrophobicity of PILs according to the observed limiting ϕ_K^0 data. This is revealed from the estimated hydration numbers of the studied PILs from compressibility data using Passynski's method[2,3] at 298.15 K as shown in Figure 11. The hydration numbers decrease with an increase in the concentration of PILs, which is due to the ion association at higher concentrations. Generally, the low-charge-density ions should not get hydrated or have negligibly small hydration numbers with very weak H-bonding, as is the case for the iodide ion. Recently, we observed large hydration numbers for amino acid ionic liquids and further showed that the observed hydration numbers are solely due to the amino acid anions, as the associated cations are only slightly hydrated.[19,59] The analysis of partial molar entropy data and enthalpy–entropy compensation effects revealed that the observed large hydration numbers for amino acid ionic liquids are due to cooperative H-bonding with and around the carboxylate functionality of amino acid anions.[19] Near-infrared (NIR) investigations for aqueous solutions of amino acid ionic liquids (AAILs) showed that water in the hydration shell of amino acid anions makes a major contribution to the icelike structure, i.e., the hydration shell of amino acid anions is highly structured.[59] Seen in this light, the observed large hydration numbers for studied PILs are due to the cooperative H-bonding of the carboxylate functional group of anions with the surrounding water. The hydration numbers of PILs at infinite dilution (Table 9) reveal that the hydration numbers increase with an increase in the hydrophobicity of the anions of PILs, and this trend exists even at the finite concentrations studied, indicating that the hydrophobic hydration existing at infinite dilution persists even at a higher concentration although ion association occurs at the highest concentration studied (Figure 11). Thus, all of these prove that the studied PILs (which are completely water-miscible) are hydrophobic ionic liquids which can dissolve hydrophobic solutes in an aqueous medium and thus can become potential candidates for drug dissolutions/formulations and in protein chemistry, since all of these PILs involve constituting cations and anions of biological origin and hence may be nontoxic or less toxic.

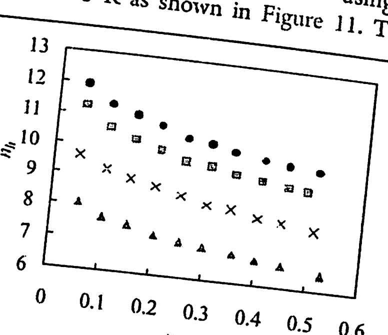

Figure 11. Variation of the hydration number (n_h) as a function of the molality (m) of ionic liquids at 298.15 K: [DEAF], ▲; [DEAA], ×; [DEAP], ■; and [DEAB], ●.

5. CONCLUSIONS

Synthesis and thermodynamic properties based on density and speed-of-sound measurements are reported for diethylammonium-based protic ionic liquids, which are also bio-ion liquids. The standard entropy (S^0) and lattice potential energ (U_{POT}) data for pure PILs at 298.15 K indicated that the lattic arrangements are more disordered for the studied PILs explaining why these bio-ionic liquids exist in the liquid state at room temperature, and are also favored by the increased hydrophobicity of PILs through increasing the alkyl chain length on the carboxylate anions. Apparent and partial molar volume analysis revealed the strengthening of the water structure around ions with hydrophobic hydration. The electrostricted hydration numbers of PILs increase not only with temperature but also with an increase in the hydrophobicity of PILs, which is strong evidence of the existence of hydrophobic hydration, as also supported in this work by compressibility data. Negative values of limiting apparent molar compressibility data indicated well-organized strong H-bonding within the hydration shell of ions, leading to a compressibility loss which increases with hydrophobicity, supporting the conclusions drawn from the temperature-dependent electrostriction effects. Compressibility-based hydration numbers are found to be largely analogous to those observed for amino acid ionic liquids and are due to cooperative H-bonding. Combined temperature, concentration, and hydrophobicity effects for the hydration numbers of the studied PILs confirm that hydrophobic hydration existing at infinite dilution persists even at the highest studied concentration, which signals hydrophobic ion association at a higher concentration rather than traditional ion pairing due to Coulombic attraction. Finally, this study highlights the hydrophobic nature of completely water-miscible diethylammonium-based carboxylate bio-ionic liquids, which can act as potential candidates for hydrophobic drug dissolution/formulation and in protein chemistry as osmolytes for the solubilization and stabilization of proteins.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00909.

^{1}H NMR spectra of synthesized PILs (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dhd_chem@unishivaji.ac.in.

ORCID

Dilip H. Dagade: 0000-0003-2517-5360

Notes

The authors declare no competing financial interest.

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