

Temperature Effect on the Molecular Interactions between Ammonium Ionic Liquids and *N,N*-Dimethylformamide

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In view of the wide scope of molecular interactions between the highly polar compound of *N,N*-dimethylformamide (DMF) and ammonium ionic liquids (ILs), we have measured thermophysical properties such as densities (ρ) and ultrasonic sound velocities (u) over the whole composition range at temperatures ranging from 25 to 50 °C under atmospheric pressure. To gain some insight into the several aggregations of molecular interactions present in these mixed solvents, we predicted the excess molar volume (V^E) and the deviations in isentropic compressibilities (ΔK_S) as a function of the concentration of IL. These results are fitted to the Redlich–Kister polynomials. The materials investigated in the present study included the hydroxide series of ammonium ILs of tetramethylammonium hydroxide [(CH₃)₄N][OH] (TMAH), tetraethylammonium hydroxide [(C₂H₅)₄N][OH] (TEAH), and tetrapropylammonium hydroxide [(C₂H₇)₄N][OH] (TPAH). The intermolecular interactions and structural effects were analyzed on the basis of the measured and the derived properties. A qualitative analysis of the results is discussed in terms of the ion–dipole and ion–pair interactions, and hydrogen bonding between ILs and DMF molecules and their structural factors.

Introduction

During the past decade, interest in the utility of environmentally friendly ionic liquids (ILs) and the broad variety of applications have increased immensely. ILs are a relatively new class of compounds that are liquid at or relatively near room temperature. These compounds appear to be the replacements for volatile organic compounds (VOCs). Due to the ionic nature of these materials, ILs have essentially insignificant vapor pressure and they therefore can be envisioned as being useful in a variety of applications.^{1,2} The development of neoteric solvents, i.e., ILs, for chemical synthesis holds great promise for green chemistry applications.³ ILs were initially synthesized in the early 20th century and at present there are over 200 types of ILs prepared. Some of these have been successfully applied in organic synthesis and other aspects.^{4–6} One of the major objectives of the chemical industry today is to search for safer alternatives of VOCs that will minimize air pollution, climatic changes, and human health-related problems. ILs exhibit certain desirable physical properties, wide electrochemical window, wide thermal window, nonflammability, wide range of densities and viscosities, high potential for recycling, and high solvating capacity for organic compounds. Their perceived status as “designer”, alternative “green” solvents has contributed largely to this interest, i.e., the existence of fluids with no measurable volatility, and are able to selectively dissolve different types of solute merely by exchanging one of the ions that form the IL, or even more subtly, by altering one of the organic residues within a given ion. Recently, our research group has demonstrated the application and limitation of ILs as solvent in chemical processes.^{7–10}

The research on ILs still is in its preliminary phase; the reasons are (i) pure ILs and mixtures containing ILs differ noticeably from so-called “normal liquids”, and their behavior is not fully understood, and (ii) new compounds with unknown properties are being synthesized. The ILs possess many unique properties as compared to ordinary fluids. On the other hand, their structures are varied with designable functions. Although the number of research articles on ILs is increasing exponentially, there is still a lack of data on their thermophysical description and molecular modeling properties. The aim is to achieve exactly the desired chemical and physical properties by a judicious combination of an anion and a cation.

The study of the properties and structure of complex liquid mixtures is necessary from both the theoretical and experimental points of view. Mixed solvents are almost ubiquitous in the industry in different fields ranging from petrochemistry to pharmaceutical industries. Thermodynamic properties of mixed solvents have been particularly informative in elucidating the solute–solute and solute–solvent interactions that exist in these solutions. Experimental data of thermodynamic and thermophysical properties of liquids and liquid mixtures are fascinating and of high fundamental, practical importance for the industry. Although a qualitative connection between the macroscopic and microscopic features is feasible, quantitative conclusions are of interest to both academic and industry communities. In spite of the importance of properties of ILs in different solvent media, only a small amount of physicochemical data is available in the literature, which mainly characterizes ILs.^{7,11–15} In this context, our aim is to explore closely two key thermophysical properties such as density (ρ) and ultrasonic sound velocity (u) for the mixed solvents of ILs and polar solvent. Till date, there is no systematic documentation for the ammonium hydroxide ILs with polar solvents. For these reasons, three ammonium ILs were synthesized in our laboratory by the simplest methods, which increase its utility. Interactions of ILs with organic molecular liquids have been rather scarcely investigated up to

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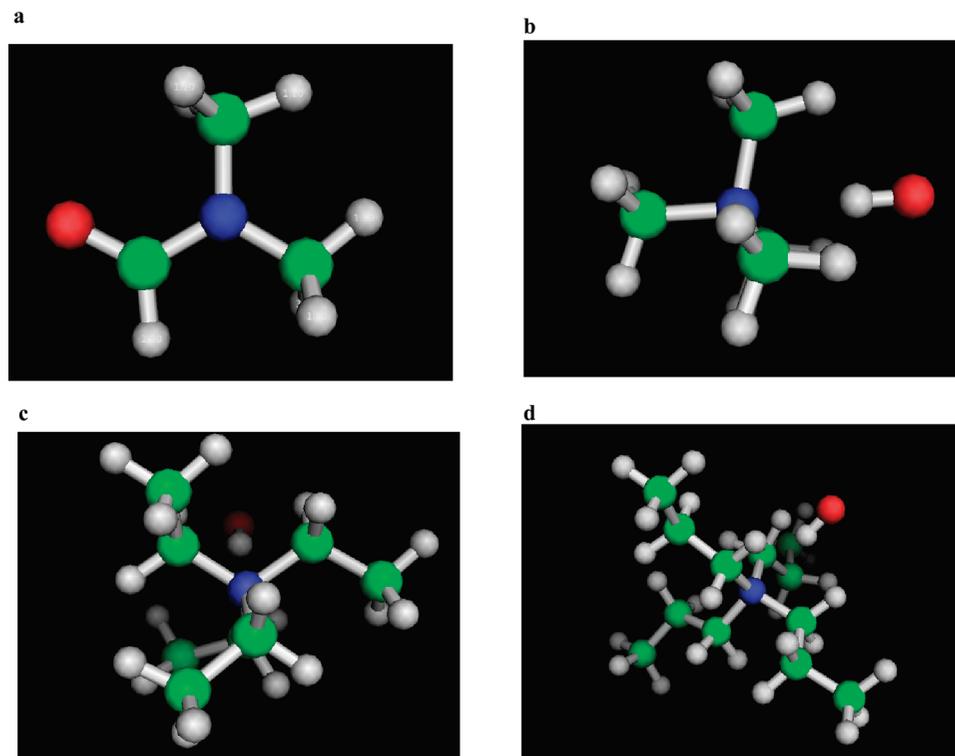
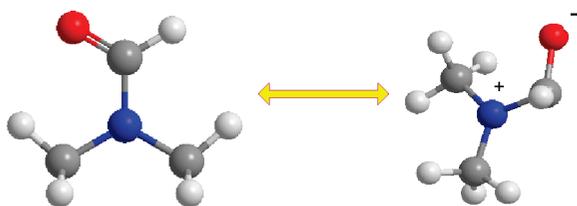


Figure 1. Schematic structures for (a) DMF, (b) TMAH, (c) TEAH, and (d) TPAH. Color representation: green = carbon, white = hydrogen, red = oxygen, and blue = nitrogen.

now on the basis of thermophysical properties and are yet to be understood clearly.

N,N-Dimethylformamide (DMF) is a polar solvent used widely in a variety of industrial processes, including manufacture of synthetic fibers, leathers, films, and surface coatings.^{16–19} DMF is a stable compound with a strong electron pair donating and accepting ability and is widely used in studies on solvent reactivity relationships.^{20–22} DMF is of particular interest because any significant structural effects are absent due to the lack of hydrogen bonds. Therefore, it may be used as an aprotic protophilic solvent with a large dipole moment, a high dielectric constant ($\mu = 3.24$ D and $\epsilon = 36.71$ at 25 °C),²³ and good donor–acceptor properties, which enable it to dissolve a wide range of both organic and inorganic substances. In addition, DMF can serve as a model compound for peptides to obtain information on protein systems. The resonance structure of DMF is shown below.



The negative pole in DMF is an oxygen atom that juts out from the rest of the molecule and this oxygen atom is the best hydrogen bond acceptor. Through their unshared pairs of electrons, these negatively charged, well-exposed atoms are solvated very strongly. The positive pole nitrogen atom, on the other hand, is buried within the molecule. In DMF, the presence of two electrons repelling $-\text{CH}_3$ groups make the lone pair at nitrogen still more perceptible toward donation.^{24,25} Thus, it may be argued that the DMF is actually the donor of nitrogen electron

pairs. The schematic chemical structures of the DMF as well as ILs are shown in Figure 1.

To characterize the type and magnitude of the molecular interactions between DMF with ILs, we herein present densities and ultrasonic sound velocities of DMF with tetramethylammonium hydroxide $[(\text{CH}_3)_4\text{N}][\text{OH}]$ (TMAH), tetraethylammonium hydroxide $[(\text{C}_2\text{H}_5)_4\text{N}][\text{OH}]$ (TEAH), and tetrapropylammonium hydroxide $[(\text{C}_2\text{H}_7)_4\text{N}][\text{OH}]$ (TPAH) at temperatures ranging from 25 to 50 °C and at atmospheric pressure over the whole composition range. No effort appears to have been made in the literature to study the molecular interactions between DMF and these ILs in terms of V^E and ΔK_s . This study intends to draw molecular level information from the macroscopic properties on the molecular interaction between ILs and DMF.

Experimental Section

Materials and Methods.

Materials. DMF (Aldrich, purity >99.9%) and tetramethylammonium bromide, tetraethylammonium bromide, and tetrapropylammonium bromide were purchased from Sigma Chemical Co., USA. The fluids were degassed with ultrasound and kept in the dark over Fluka 0.3 nm molecular sieves for several days and purified by fractional distillation. The purity of the chemical products was verified by measuring the densities (ρ), refractive indices (n), and sound velocity (u), which were in good agreement with the literature values.²³ The purities of the samples were further confirmed by the GLC single sharp peaks. All ILs were synthesized²⁶ in our laboratory, as given below.

Synthesis of ILs. The ammonium hydroxide series of ILs used in this study, namely TMAH, TEAH, and TPAH were synthesized in the following manner.

Synthesis of Tetramethylammonium Hydroxide (TMAH). The synthesis of this IL was carried out in a 250 mL round-bottomed flask, which was immersed in a water bath and fitted with a reflux condenser. Solid potassium hydroxide (40 mmol)

was added to a solution of tetramethylammonium bromide $[(\text{CH}_3)_4\text{N}][\text{Br}]$ (40 mmol) in dry methylene chloride (20 mL), and the mixture was stirred vigorously at room temperature for 10 h. The precipitated KBr was filtered off, and the filtrate was evaporated to leave the crude $[(\text{CH}_3)_4\text{N}][\text{OH}]$ as a viscous liquid that was washed with ether (2×20 mL) and dried at 70°C for 5 h to obtain the pure IL. The sample was analyzed by Karl Fisher titration which revealed very low levels of water (below 70 ppm). The yield of TMAH was 68%. $^1\text{H NMR}$ (DMSO- d_6): δ (ppm) 2.38 (s, 12H), 4.79 (s, OH). HRMS calculated for $\text{C}_4\text{H}_{13}\text{NO}$ ($\text{M}^+ - \text{OH}$) 91.15, found 91.09.

Synthesis of Tetraethylammonium Hydroxide (TEAH). A similar procedure as delineated above for $[(\text{C}_2\text{H}_5)_4\text{N}][\text{OH}]$ was followed with the exception of the use of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Br}]$ ([cation]) instead of $[(\text{CH}_3)_4\text{N}][\text{Br}]$. The yield of TEAH was 78%. $^1\text{H NMR}$ (DMSO- d_6): δ (ppm) 1.01 (t, 12H), 3.06 (q, 8H), 4.43 (s, OH). HRMS calculated for $\text{C}_8\text{H}_{21}\text{NO}$ ($\text{M}^+ - \text{OH}$) 147.26, found 147.20.

Synthesis of Tetrapropylammonium Hydroxide (TPAH). A procedure similar to that above for $[(\text{CH}_3)_4\text{N}][\text{OH}]$ was followed with the exception of the use of $[(\text{C}_3\text{H}_7)_4\text{N}][\text{Br}]$ ([cation]) instead of $[(\text{CH}_3)_4\text{N}][\text{Br}]$. The yield of TPAH was 82%. $^1\text{H NMR}$ (DMSO- d_6): δ (ppm) 0.8 (t, 12H), 1.46 (m, 8H), 2.92 (t, 8H), 4.56 (s, OH). HRMS calculated for $\text{C}_{12}\text{H}_{29}\text{NO}$ ($\text{M}^+ - \text{OH}$) 203.36, found 203.25.

Methods. The density measurements were performed with an Anton-Paar DMA 4500 M vibrating-tube densimeter, equipped with a built-in solid-state thermostat and a resident program with accuracy of temperature of $\pm 0.03^\circ\text{C}$. Typically, density precisions are 0.00005 g cm^{-3} . Proper calibration at each temperature was achieved with doubly distilled, deionized water and with air as standards. The excess molar volumes (V^E) ($\pm 0.003\text{ cm}^3\text{ mol}^{-1}$) were deduced from the densities of the pure compounds and mixture (ρ_m) using the standard equations. Ultrasonic sound velocities were measured by a single-crystal ultrasonic interferometer (model F-05) from Mittal Enterprises, New Delhi, India, at 2 MHz frequency at various temperatures. A thermostatically controlled, well-stirred circulated water bath with temperature controlled to $\pm 0.01^\circ\text{C}$ was used for all the ultrasonic sound velocity measurements. The uncertainty in sound velocity is 0.02%. ^1H (400 MHz) spectra were recorded on a JEOL 400 NMR spectrometer in DMSO- d_6 . The reactions were monitored by thin layer chromatography (TLC) using aluminum sheets with silica gel 60 F254 (Merck). Clear solutions were prepared gravimetrically using a Mettler Toledo balance with a precision of $\pm 0.0001\text{ g}$. The uncertainty in solution composition expressed in mole fraction was found to be less than 5×10^{-4} . Mixing of the two components was promoted by the movement of a small glass sphere (inserted in the vial prior to the addition of the ILs) as the flask was slowly and repeatedly inverted. After sample was mixed, the bubble-free homogeneous sample was transferred into the U-tube of the densimeter or the sample cell of ultrasonic interferometer through a syringe.

Results and Discussion

To understand the molecular interactions of DMF with the alkyl series of the hydroxide family of ammonium ILs, we have measured the thermophysical properties such as ρ and u over the entire composition range at temperature ranging from 25 to 50°C under atmospheric pressure. In reality, ILs are miscible with medium to high dielectric liquids and immiscible with low dielectric liquids.²⁷ In the present study, all ILs are completely miscible in DMF ($\epsilon = 36.71$ at 25°C),²³ since DMF is a high

dielectric liquid. Experimental values of ρ and u at various temperatures are collected in Table 1 for ILs, DMF, and their mixtures over the whole composition range. It was found that the ρ or u of the mixtures increases with increasing concentrations of the IL in DMF, as shown in Figures 2 and 3, respectively. The effect of the ILs on the ρ and u in the DMF has been examined at various temperatures. As it can be observed, the ρ and u sharply decrease as the temperature increases in the three systems. For the sake of clarity and comparison between three ILs, the ρ and u values of IL + DMF over the whole composition range at 25°C have been presented in Figure 4. The results in Figure 4a clearly show that the density values of the TEAH + DMF mixtures are higher when compared to the values for mixtures of the TMAH + DMF and TPAH + DMF. However, the TMAH + DMF mixtures have higher ρ values at very rich IL concentration ≈ 0.9600 . The density of all the ILs increases as the mole fraction of IL increases up to 0.6000. A drastic change in ρ was found in the case of TMAH + DMF at the mole fraction of TMAH 0.6000–0.9000, which may be due to the increased intermolecular interaction between the TMAH and DMF. However, in the case of TPAH or TEAH, there is a sharp decrease in ρ . In other words, we can state that the density does not increase sharply at mole fraction 0.6000–0.9000, which may be due to a decrease in the ion-pair interaction between these ILs and DMF. The density generally decreases with increasing length of alkyl chain in a cation or anion as documented earlier for ILs.^{28,29} Interestingly, this conclusion is not consistent with the observations of the present study. The experimental results described that the densities of investigated systems increase with increasing the length of alkyl chain in IL. We observed the ρ values to be higher in the TEAH mixture, lower in the TMAH, and moderate in the TPAH at equimolar mixture. These discrepancies vary from IL to IL and solvent to solvent and also depend on the nature as well as structural arrangement of IL and solvent.

Ultrasonic sound velocities are also another important source of information about the properties of different solvents and their mixture. The values of u were found to decrease with an increase in temperature while u values increase with increasing mole fraction of IL. As noted from Figure 3, there is a sharp increase of u in all ILs, except in the mixture of TEAH or TPAH with DMF at the mole fraction range from 0.4000 to 0.9900 of IL. At this range the u values increase slightly for the mixtures of TEAH or TPAH with DMF at all investigated temperatures. By addition of TEAH to DMF, u values increase rapidly up to ≈ 0.4000 of IL and finally slightly increase to the corresponding value in TEAH through a maximum at $X_{\text{IL}} = 0.9000$ (Figure 4b). This u value is significantly increased in IL–solvent interactions when the mole fraction of IL increases. Fascinating results are seen in the case of TPAH for which its u value at 30°C is higher than that at 25°C , while a decrease is noted when higher mole fraction is reached. This may be due to the self-interaction occurring between the TPAH molecules at 30°C . As seen from Figure 4b, the sound velocity of TMAH or TEAH with DMF at 25°C increases with increasing composition of IL. On the other hand, in the case of TPAH with DMF, there is a rapid increase in u values up to the mole fraction ≈ 0.6000 of TPAH, with the values sharply increasing up to mole fraction 0.9900 of TPAH. As seen from the results in Figure 4b, it is clear that there is no regular order in the values of u for the ILs with DMF and this may be due to the large steric hindrance in the bulky groups, which tends to resist crowding more than smaller groups. The TPAH IL exhibits a higher u values up to

TABLE 1: Mole Fraction (x_1) of ILs, Density (ρ), Ultrasonic Sound Velocity (u), Isentropic Compressibility (K_s), and Deviation in Isentropic Compressibility (ΔK_s) for the Systems of ILs with DMF at Various Temperatures and at Atmospheric Pressure

x_1	$\rho/\text{g cm}^{-3}$	$u/\text{m s}^{-1}$	$V^E/\text{cm}^{-3} \text{ mol}^{-1}$	K_s/TPa^{-1}	$\Delta K_s/\text{TPa}^{-1}$	x_1	$\rho/\text{g cm}^{-3}$	$u/\text{m s}^{-1}$	$V^E/\text{cm}^{-3} \text{ mol}^{-1}$	K_s/TPa^{-1}	$\Delta K_s/\text{TPa}^{-1}$
TMAH with DMF at 25 °C											
0	0.94385	1456	0	500	0	0.7076	0.98596	1785	1.103	318	-35.7
0.1034	0.95418	1502	-0.091	464	-14.4	0.7875	0.98913	1804	1.311	311	-26.9
0.2119	0.96464	1561	-0.229	425	-30.7	0.8501	0.99376	1811	1.277	306	-18.1
0.3262	0.97330	1619	-0.207	392	-40.8	0.9166	0.99980	1820	1.133	302	-9.1
0.4465	0.97740	1680	0.214	362	-45.4	1	1.01797	1828	0	294	0
0.5735	0.98252	1737	0.572	337	-44.3						
TMAH with DMF at 30 °C											
0	0.94028	1424	0	524	0	0.7076	0.98427	1788	1.007	318	-46.8
0.1034	0.95413	1492	-0.414	471	-30.3	0.7875	0.98750	1804	1.222	311	-35.3
0.2119	0.96602	1551	-0.656	430	-46.4	0.8501	0.99190	1805	1.218	309	-22.7
0.3262	0.97498	1615	-0.644	393	-57.6	0.9166	0.99980	1811	0.916	305	-12.5
0.4465	0.97993	1679	-0.282	362	-61.9	1	1.01564	1817	0	298	0
0.5735	0.98213	1742	0.342	335	-59.2						
TMAH with DMF at 35 °C											
0	0.93552	1392	0	552	0	0.7076	0.98192	1790	0.948	318	-57.9
0.1034	0.95171	1463	-0.592	490	-35.5	0.7875	0.98576	1801	1.125	313	-42.8
0.2119	0.96470	1538	-0.905	438	-60.7	0.8501	0.99050	1802	1.105	311	-29.2
0.3262	0.97326	1607	-0.838	398	-72.8	0.9166	0.99851	1804	0.802	308	-15.7
0.4465	0.97784	1685	-0.419	360	-80.6	1	1.01321	1806	0	303	0
0.5735	0.98064	1744	0.179	335	-73.8						
TMAH with DMF at 40 °C											
0	0.93098	1360	0	581	0	0.7076	0.98197	1767	0.669	326	-61.1
0.1034	0.94821	1434	-0.683	512	-40.2	0.7875	0.98439	1785	0.987	319	-46.7
0.2119	0.96190	1522	-1.035	448	-74.3	0.8501	0.98902	1786	0.986	317	-31.2
0.3262	0.97187	1614	-1.065	395	-96.8	0.9166	0.99676	1790	0.722	313	-16.8
0.4465	0.97753	1697	-0.715	355	-103.3	1	1.01071	1795	0	307	0
0.5735	0.97990	1760	-0.0549	329	-94.5						
TMAH with DMF at 45 °C											
0	0.92595	1327	0	613	0	0.7076	0.98190	1760	0.394	328	-71.3
0.1034	0.94477	1401	-0.784	539	-43.2	0.7875	0.98490	1769	0.676	324	-51.5
0.2119	0.95937	1496	-1.192	466	-83.8	0.8501	0.98909	1779	0.724	319	-37.4
0.3262	0.96937	1602	-1.203	402	-113.2	0.9166	0.99561	1781	0.582	316	-20.3
0.4465	0.97584	1681	-0.898	363	-116.0	1	1.00815	1784	0	312	0
0.5735	0.97936	1757	-0.313	330	-109.9						
TMAH with DMF at 50 °C											
0	0.92113	1295	0	647	0	0.7076	0.98210	1745	0.089	334	-79.0
0.1034	0.94189	1388	-0.936	551	-62.5	0.7875	0.98520	1767	0.375	325	-61.7
0.2119	0.95657	1476	-1.334	479	-97.7	0.8501	0.98939	1769	0.435	323	-43.0
0.3262	0.96682	1573	-1.344	418	-121.7	0.9166	0.99434	1770	0.447	321	-23.1
0.4465	0.97350	1650	-1.031	377	-122.5	1	1.00553	1773	0	316	0
0.5735	0.97856	1732	-0.554	340	-117.0						
TEAH with DMF at 25 °C											
0	0.94385	1456	0	500	0	0.5501	0.99274	1679	-0.394	357	-33.4
0.0687	0.96206	1480	-0.833	474	-11.6	0.7042	0.99258	1737	0.569	334	-26.4
0.1560	0.97937	1511	-1.646	447	-21.6	0.7836	0.99450	1764	0.803	323	-21.4
0.2172	0.98662	1535	-1.878	430	-26.8	0.8607	0.99782	1789	0.807	313	-15.7
0.2784	0.99083	1561	-1.878	414	-30.7	0.9138	1.00119	1800	0.637	308	-10.1
0.4007	0.99385	1615	-1.426	386	-34.5	1	1.00881	1814	0	301	0
TEAH with DMF at 30 °C											
0	0.94028	1424	0	524	0	0.5501	0.99647	1687	-0.978	354	-50.8
0.0687	0.96073	1469	-1.039	485	-25.0	0.7042	0.99613	1735	0.0185	335	-36.3
0.1560	0.97856	1506	-1.862	450	-40.6	0.7836	0.99719	1756	0.372	327	-27.1
0.2172	0.98626	1539	-2.1127	429	-48.8	0.8607	0.99958	1775	0.518	320	-17.9
0.2784	0.99129	1569	-2.168	410	-53.9	0.9138	1.00204	1786	0.488	314	-11.7
0.4007	0.99634	1628	-1.889	381	-56.9	1	1.00881	1803	0	307	0
TEAH with DMF at 35 °C											
0	0.93552	1392	0	552	0	0.5501	0.99387	1696	-1.245	350	-69.1
0.0687	0.95836	1446	-1.255	499	-36.1	0.7042	0.99352	1738	-0.264	333	-48.3
0.1560	0.97529	1502	-2.016	454	-59.6	0.7836	0.99456	1758	0.0817	325	-37.1
0.2172	0.98267	1542	-2.245	428	-71.2	0.8607	0.99688	1768	0.226	321	-23.0
0.2784	0.98813	1575	-2.347	408	-76.6	0.9138	0.99886	1779	0.257	316	-14.8
0.4007	0.99327	1638	-2.089	375	-79.8	1	1.00396	1792	0	310	0
TEAH with DMF at 40 °C											
0	0.93098	1360	0	581	0	0.5501	0.99258	1718	-1.484	341	-108.5
0.0687	0.95355	1444	-1.243	503	-59.1	0.7042	0.99253	1756	-0.522	327	-68.4
0.1560	0.97305	1529	-2.214	439	-101.3	0.7836	0.99323	1767	-0.124	322	-50.8
0.2172	0.98118	1588	-2.503	404	-119.4	0.8607	0.99533	1769	0.059	321	-33.9
0.2784	0.98666	1638	-2.601	377	-129.3	0.9138	0.99699	1776	0.142	318	-19.1
0.4007	0.99189	1675	-2.338	359	-129.8	1	1.00138	1781	0	315	0
TEAH with DMF at 45 °C											
0	0.92595	1328	0	612	0	0.5501	0.99067	1728	-1.660	338	-108.5
0.0687	0.94993	1405	-1.336	533	-59.1	0.7042	0.99090	1743	-0.711	332	-68.4
0.1560	0.97094	1485	-2.429	467	-101.3	0.7836	0.99203	1747	-0.358	330	-50.8
0.2172	0.97937	1534	-2.738	434	-119.4	0.8607	0.99365	1748	-0.101	329	-33.3
0.2784	0.98476	1592	-2.819	401	-129.3	0.9138	0.99528	1754	-0.007	326	-19.1
0.4007	0.98993	1661	-2.532	366	-129.8	1	0.99873	1771	0	319	0

TABLE 1: Continued

x_1	$\rho/\text{g cm}^{-3}$	$u/\text{m s}^{-1}$	$V^E/\text{cm}^{-3} \text{mol}^{-1}$	K_s/TPa^{-1}	$\Delta K_s/\text{TPa}^{-1}$	x_1	$\rho/\text{g cm}^{-3}$	$u/\text{m s}^{-1}$	$V^E/\text{cm}^{-3} \text{mol}^{-1}$	K_s/TPa^{-1}	$\Delta K_s/\text{TPa}^{-1}$
TEAH with DMF at 50 °C											
0	0.92113	1296	0	646	0	0.5501	0.98876	1706	-1.848	347	-122.2
0.0687	0.94667	1372	-1.465	561	-63.2	0.7042	0.98948	1722	-0.938	341	-78.8
0.1560	0.96774	1454	-2.552	489	-107.5	0.7836	0.99000	1727	-0.495	339	-55.6
0.2172	0.97636	1518	-2.869	444	-131.9	0.8607	0.99190	1733	-0.265	336	-33.7
0.2784	0.98185	1571	-2.949	412	-144.3	0.9138	0.99348	1741	-0.159	332	-20.4
0.4007	0.98732	1653	-2.669	370	-146.9	1	0.99598	1759	0	325	0
TPAH with DMF at 25 °C											
0	0.94385	1456	0	500	0	0.4964	0.98570	1730	-1.160	339	-66.7
0.0725	0.95948	1499	-0.874	463	-22.5	0.6746	0.98558	1756	-0.403	329	-42.6
0.1560	0.97037	1562	-1.370	422	-47.9	0.7943	0.98629	1764	0.0345	326	-22.8
0.2145	0.97640	1605	-1.598	397	-61.5	0.8554	0.98789	1772	0.145	322	-14.8
0.2784	0.98059	1643	-1.661	378	-69.3	0.9299	0.99096	1789	0.172	315	-7.6
0.3422	0.98346	1676	-1.624	362	-72.9	1	0.99594	1801	0	310	0
TPAH with DMF at 30 °C											
0	0.94028	1424	0	524	0	0.4964	0.98353	1722	-1.256	343	-75.1
0.0725	0.95602	1480	-0.926	477	-28.6	0.6746	0.98368	1754	-0.492	330	-52.2
0.1560	0.96768	1562	-1.475	424	-55.	0.7943	0.98535	1766	-0.122	325	-32.3
0.2145	0.97377	1606	-1.699	398	-66.7	0.8554	0.98678	1780	0.012	320	-20.9
0.2784	0.97802	1646	-1.758	377	-75.4	0.9299	0.98979	1782	0.055	318	-8.5
0.3422	0.98112	1685	-1.729	359	-79.1	1	0.99360	1790	0	314	0
TPAH with DMF at 35 °C											
0	0.93552	1392	0	552	0	0.4964	0.98072	1721	-1.329	344	-92.1
0.0725	0.95203	1446	-0.983	502	-33.0	0.6746	0.98163	1749	-0.596	333	-61.9
0.1560	0.96386	1523	-1.533	447	-68.6	0.7943	0.98348	1756	-0.218	330	-37.1
0.2145	0.97025	1571	-1.772	417	-84.3	0.8554	0.98503	1763	-0.083	327	-25.9
0.2784	0.97448	1619	-1.818	391	-95.5	0.9299	0.98790	1772	-0.013	322	-12.8
0.3422	0.97779	1657	-1.793	372	-99.6	1	0.99111	1779	0	319	0
TPAH with DMF at 40 °C											
0	0.93098	1360	0	581	0	0.4964	0.97654	1721	-1.422	345	-108.0
0.0725	0.94794	1438	-1.054	510	-52.7	0.6746	0.97814	1739	-0.753	338	-69.6
0.1560	0.95977	1523	-1.614	449	-92.2	0.7943	0.97935	1753	-0.322	332	-44.7
0.2145	0.96609	1576	-1.854	416	-109.5	0.8554	0.98076	1759	-0.177	330	-31.7
0.2784	0.97021	1623	-1.893	391	-118.2	0.9299	0.98321	1762	-0.072	328	-14.5
0.3422	0.97373	1661	-1.890	372	-120.8	1	0.98576	1769	0	324	0
TPAH with DMF at 45 °C											
0	0.92595	1327	0	613	0	0.4964	0.97585	1699	-1.567	355	-116.9
0.0725	0.94431	1410	-1.130	533	-60.0	0.6746	0.97813	1738	-0.884	338	-82.4
0.1560	0.95643	1495	-1.681	468	-101.2	0.7943	0.98017	1753	-0.479	332	-54.7
0.2145	0.96309	1546	-1.924	434	-117.9	0.8554	0.98167	1758	-0.319	330	-39.5
0.2784	0.96766	1593	-1.974	407	-126.7	0.9299	0.98399	1750	-0.172	329	-16.2
0.3422	0.97153	1634	-1.973	385	-130.4	1	0.98576	1759	0	328	0
TPAH with DMF at 50 °C											
0	0.92113	1296	0	646	0	0.4964	0.97279	1668	-1.643	369	-121.9
0.0725	0.94039	1386	-1.204	553	-70.7	0.6746	0.97588	1726	-0.999	344	-91.5
0.1560	0.95342	1465	-1.821	488	-109.0	0.7943	0.97832	1733	-0.609	340	-57.4
0.2145	0.95984	1511	-2.036	456	-122.9	0.8554	0.97974	1744	-0.430	335	-43.2
0.2784	0.96489	1558	-2.116	427	-132.5	0.9299	0.98196	1746	-0.262	334	-21.2
0.3422	0.96844	1599	-2.076	403	-135.8	1	0.98291	1747	0	333	0

≈ 0.5800 mol fraction of TPAH than TMAH or TEAH with DMF at 25 °C. Later, the u values of TPAH sharply decrease from 0.6000 to 0.9800 mol fraction TPAH and obviously the u values are lower than those of TMAH or TEAH with DMF. This is a somewhat surprising result, since one would expect at first view that, as the side chain length increases, the overall contribution will generally increase. This shows that there is a significant effect of ρ on the u ; as the density increases, the sound velocity also increases.

Thermophysical properties of mixed solvents of ILs with DMF can be tunable. The extent of deviation of liquid mixtures from ideal behavior is best expressed by excess functions. Among them, the excess volumes can be interpreted in three areas, namely physical, chemical, and structural effects.⁷ In recent years the ultrasonic studies have been adequately employed in understanding the nature of molecular interaction in solvent mixed systems. In the chemical industry, a knowledge of the ultrasonic and its related properties of solutions is essential in the design involving chemical separation, heat transfer, mass transfer, and fluid flow. Isentropic compressibilities (K_s) of the binary mixtures were calculated using the relation from ρ and u . The detailed procedure of obtaining of K_s and deviation in

isentropic compressibilities (ΔK_s) are delineated in our previous article.⁷ The composition dependence of the V^E and ΔK_s properties represents the deviation from ideal behavior of the mixtures and provides an indication of the interactions between IL and DMF. These properties were mathematically fitted by variable degree functions using the Redlich–Kister expression:

$$Y = x_1 x_2 \left(\sum_{i=0}^n a_i (x_1 - x_2)^i \right) \quad (1)$$

where Y refers to V^E or ΔK_s , a_i are adjustable parameters and can be obtained by least-squares analysis. Values of the fitted parameters are listed in Table 2 along with the standard deviations of the fit. The values of V^E and ΔK_s for the binary mixtures at various temperatures as function of ILs concentrations are included in Table 1. Figures 5 and 6 display the experimental data for the binary mixtures, and the fitted curves, along with the excess properties of V^E and ΔK_s for the DMF with ILs as function of IL concentrations at different temperatures.

Graphical representations in Figure 5 exhibit an inversion in sign of the excess volumes for the binary mixtures of ILs with

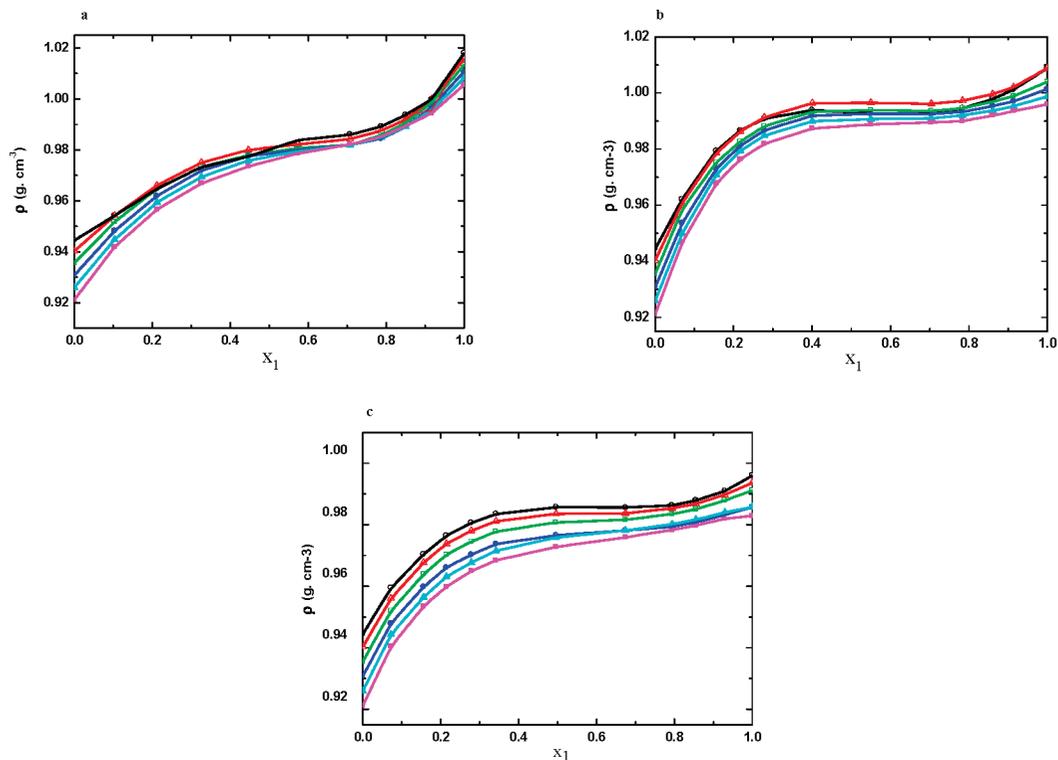


Figure 2. Densities for the mixtures of ILs with DMF vs mole fraction of IL x_1 for (a) TMAH $\{(x_1) 25\text{ }^\circ\text{C} (\text{O}) +, \text{ or } (x_1) 30\text{ }^\circ\text{C} (\Delta) +, \text{ or } (x_1) 35\text{ }^\circ\text{C} (\square) +, \text{ or } (x_1) 40\text{ }^\circ\text{C} (\bullet) +, \text{ or } (x_1) 45\text{ }^\circ\text{C} (\blacktriangle) +, \text{ or } (x_1) 50\text{ }^\circ\text{C} (\blacksquare) + \text{DMF } (x_2)\}$; (b) TEAH $\{(x_1) 25\text{ }^\circ\text{C} (\text{O}) +, \text{ or } (x_1) 30\text{ }^\circ\text{C} (\Delta) +, \text{ or } (x_1) 35\text{ }^\circ\text{C} (\square) +, \text{ or } (x_1) 40\text{ }^\circ\text{C} (\bullet) +, \text{ or } (x_1) 45\text{ }^\circ\text{C} (\blacktriangle) +, \text{ or } (x_1) 50\text{ }^\circ\text{C} (\blacksquare) + \text{DMF } (x_2)\}$; and (c) TPAH $\{(x_1) 25\text{ }^\circ\text{C} (\text{O}) +, \text{ or } (x_1) 30\text{ }^\circ\text{C} (\Delta) +, \text{ or } (x_1) 35\text{ }^\circ\text{C} (\square) +, \text{ or } (x_1) 40\text{ }^\circ\text{C} (\bullet) +, \text{ or } (x_1) 45\text{ }^\circ\text{C} (\blacktriangle) +, \text{ or } (x_1) 50\text{ }^\circ\text{C} (\blacksquare) + \text{DMF } (x_2)\}$ at various compositions and at atmospheric pressure. The solid line represents the smoothness of these data.

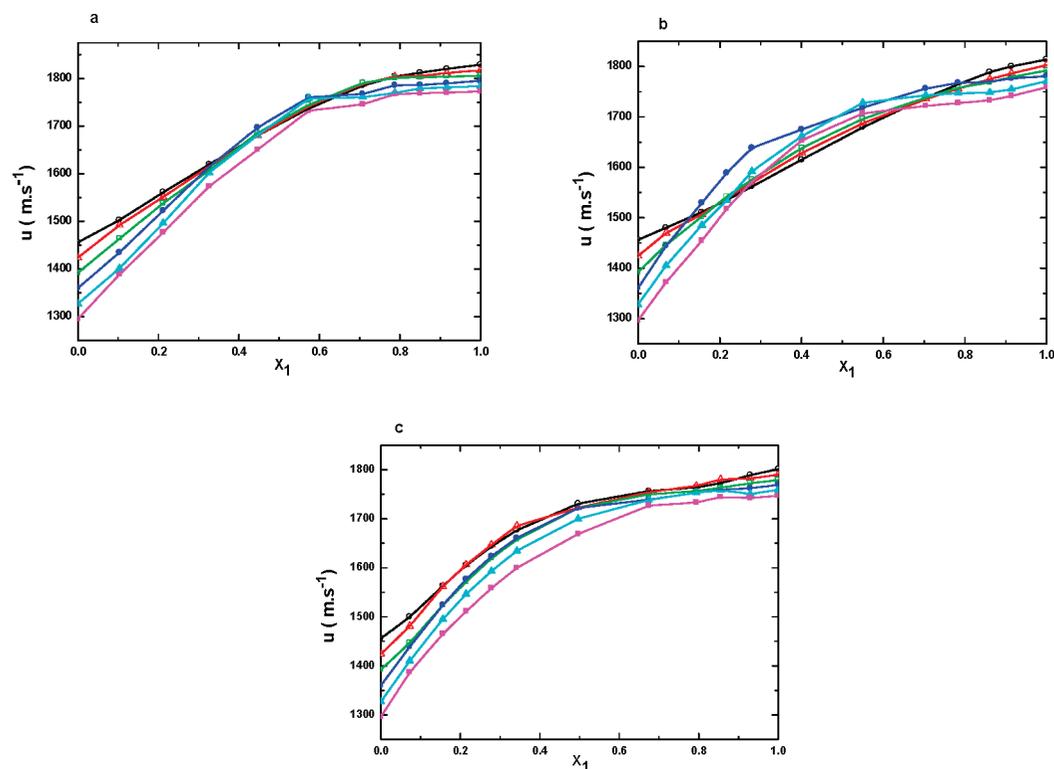


Figure 3. Ultrasonic sound velocity for the mixtures of ILs with DMF vs mole fraction of IL x_1 for (a) TMAH $\{(x_1) 25\text{ }^\circ\text{C} (\text{O}) +, \text{ or } (x_1) 30\text{ }^\circ\text{C} (\Delta) +, \text{ or } (x_1) 35\text{ }^\circ\text{C} (\square) +, \text{ or } (x_1) 40\text{ }^\circ\text{C} (\bullet) +, \text{ or } (x_1) 45\text{ }^\circ\text{C} (\blacktriangle) +, \text{ or } (x_1) 50\text{ }^\circ\text{C} (\blacksquare) + \text{DMF } (x_2)\}$; (b) TEAH $\{(x_1) 25\text{ }^\circ\text{C} (\text{O}) +, \text{ or } (x_1) 30\text{ }^\circ\text{C} (\Delta) +, \text{ or } (x_1) 35\text{ }^\circ\text{C} (\square) +, \text{ or } (x_1) 40\text{ }^\circ\text{C} (\bullet) +, \text{ or } (x_1) 45\text{ }^\circ\text{C} (\blacktriangle) +, \text{ or } (x_1) 50\text{ }^\circ\text{C} (\blacksquare) + \text{DMF } (x_2)\}$; and (c) TPAH $\{(x_1) 25\text{ }^\circ\text{C} (\text{O}) +, \text{ or } (x_1) 30\text{ }^\circ\text{C} (\Delta) +, \text{ or } (x_1) 35\text{ }^\circ\text{C} (\square) +, \text{ or } (x_1) 40\text{ }^\circ\text{C} (\bullet) +, \text{ or } (x_1) 45\text{ }^\circ\text{C} (\blacktriangle) +, \text{ or } (x_1) 50\text{ }^\circ\text{C} (\blacksquare) + \text{DMF } (x_2)\}$ at various compositions and at atmospheric pressure. The solid line represents the smoothness of these data.

DMF at all investigated temperatures and the V^E variations as a function of the composition described in an S shape. We have

observed that the excess molar volumes present a minimum at $x_1 \approx 0.22$ and a maximum at $x_1 \approx 0.78$ for the two systems of

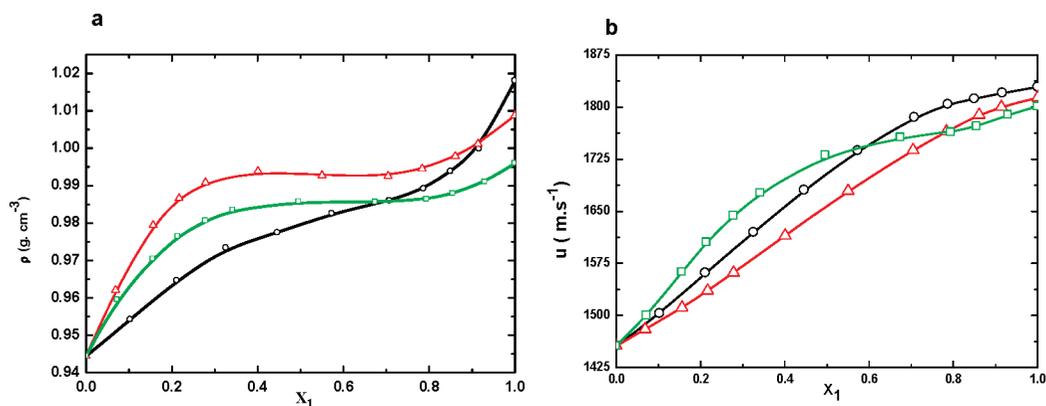


Figure 4. (a) Densities for the mixtures of ILs with DMF vs mole fraction of IL x_1 for TMAH (○), TEAH (△), and TPAH (□) at 25 °C. (b) Ultrasonic sound velocity for the mixtures of ILs with DMF vs mole fraction of IL x_1 for TMAH (○), TEAH (△), and TPAH (□) at 25 °C.

TABLE 2: Estimated Parameters of Eq 1 and Standard Deviation σ for the Systems of ILs with DMF at Various Temperatures

Y	systems	T/°C	estimated parameters (cm ³ mol ⁻¹)					σ
			a_0	a_1	a_2	a_3	a_4	
V^E	TMAH + DMF	25	-0.0092	-0.0117	-11.0004	37.7667	-26.6811	0.002
		30	-0.0667	-3.7641	-0.30165	27.5123	-23.3662	0.004
		35	0.0007	-7.0609	11.5046	12.1359	-16.5920	0.003
		40	-0.0049	-7.5883	9.9762	16.0366	-18.4326	0.001
		45	-0.0084	-8.9485	15.0539	6.9919	-13.0869	0.002
	TEAH + DMF	25	0.0523	-17.2253	44.9733	-27.5482	-0.2713	0.002
		30	-0.0072	-17.7054	41.6563	-22.0119	-1.9212	0.002
		35	-0.0481	-19.3982	48.8524	-34.5349	5.1331	0.001
		40	-0.0060	-21.4879	54.1775	-40.7588	8.0780	0.003
		45	0.0079	-24.0789	63.7815	-54.5478	14.8389	0.003
	TPAH + DMF	25	-0.0144	-25.3051	68.3485	-61.8528	18.8209	0.002
		30	-0.0478	-18.1155	51.1391	-51.4844	18.5044	0.001
		35	-0.0164	-14.5731	37.2434	-29.1343	6.4815	0.004
		40	-0.0221	-15.3148	40.3072	-34.1854	9.2149	0.003
		45	-0.0342	-16.0159	42.7484	-38.1098	11.4182	0.002
ΔK_s	TMAH + DMF	25	-0.0456	-16.7175	45.4083	-42.8609	14.2172	0.002
		30	-0.0413	-18.4027	52.3529	-53.3211	19.4127	0.003
		25	0.18	-149.54	-33.54	401.07	-217.73	2
		30	-1.15	-294.25	374.75	-37.22	-41.02	2
		35	-0.61	-373.62	443.32	34.90	-103.25	1
	TEAH + DMF	40	0.37	-428.66	224.69	713.48	-511.04	1
		45	1.03	-476.40	179.55	930.94	-636.98	2
		50	-1.13	-663.45	992.25	-258.20	-69.23	1
		25	-0.11	-183.49	317.06	-211.77	78.18	1
		30	-1.23	-358.65	737.52	-535.09	157.58	1
	TPAH + DMF	35	-1.53	-538.11	1183.68	-935.43	291.87	1
		40	-1.59	-716.33	1411.49	-874.61	181.38	2
		45	-1.38	-938.32	2141.64	-1692.92	491.01	1
		50	-1.36	-983.26	2033.44	-1316.65	267.70	2
		25	1.64	-417.69	617.21	-21.97	-180.43	1
	30	0.26	-465.26	775.95	-274.29	-36.32	1	
	35	1.88	-603.62	1046.29	-415.51	-30.16	1	
	40	0.06	-862.99	1964.81	-1551.93	449.98	2	
	45	-1.16	-938.45	2218.39	-1927.66	650.43	1	
	50	-3.82	-999.86	2479.88	-2320.56	846.44	1	

TMAH or TEAH with DMF at all investigated temperatures, whereas we obtained that the V^E values present a minimum at $x_1 \approx 0.28$ and a maximum at $x_1 \approx 0.92$ for the systems of TPAH with DMF. The minimum increases and the maximum decreases as temperature increases for all three systems. This behavior can be explained because hydrogen bonding is certainly more T-dependent than Coulombic interactions. The minimum can be due to hydrogen bonds between DMF molecules and IL. At higher concentrations of IL, we can observe a maximum due to the dissociation of the ions forming the ILs and loss of dipolar interactions of DMF. The enormous behavior of the IL is

because it belongs to the alkyl chain of ammonium family. The V^E values clearly reveal that an inversion in the sign from negative to positive deviation means the interaction between IL and DMF decreases as the concentration of IL increases. Moreover, the V^E values are positive for IL-rich compositions and negative for DMF-rich compositions for the mixture of TMAH with DMF at all investigated temperatures. The decrease in the magnitude of the negative V^E values with an increase in IL composition can be attributed to the decrease of hydrogen bonding. Although it can also be understood as an increase in the concentration of the IL, a decrease of packing efficiency

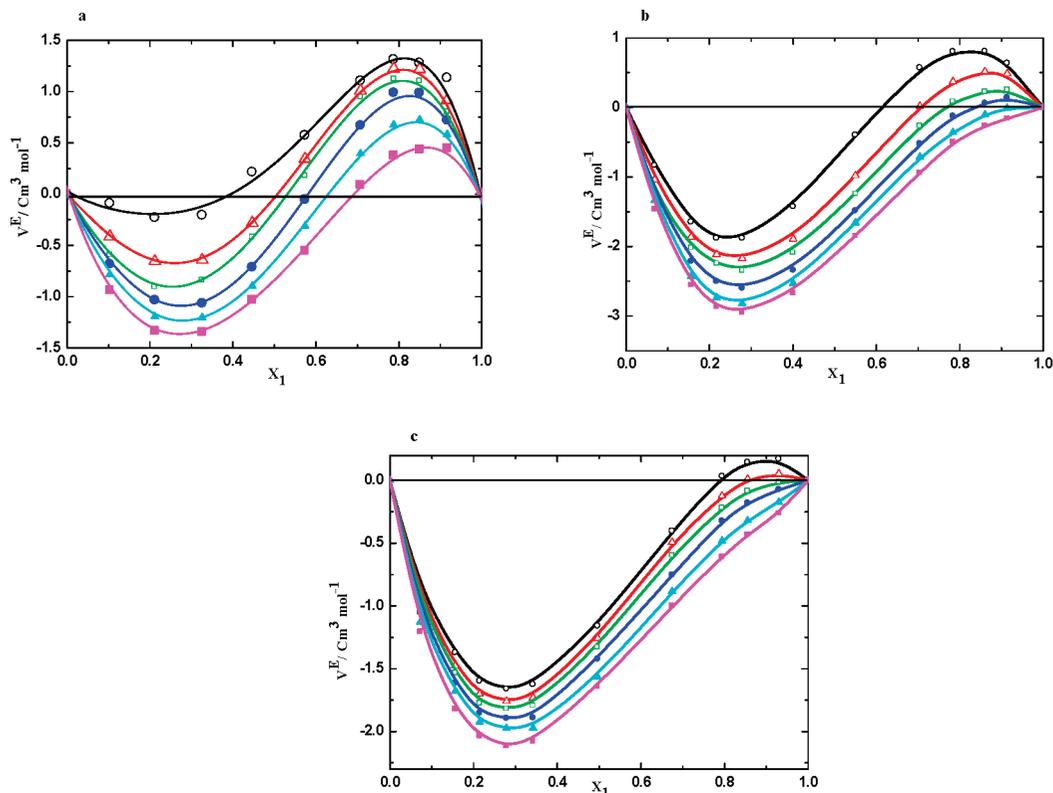


Figure 5. Excess molar volumes (V^E) against the mole fraction of ILs (a) TMAH $\{(x_1) 25\text{ }^\circ\text{C}$ (\circ) +, or $(x_1) 30\text{ }^\circ\text{C}$ (Δ) +, or $(x_1) 35\text{ }^\circ\text{C}$ (\square) +, or $(x_1) 40\text{ }^\circ\text{C}$ (\bullet) +, or $(x_1) 45\text{ }^\circ\text{C}$ (\blacktriangle) +, or $(x_1) 50\text{ }^\circ\text{C}$ (\blacksquare) + DMF (x_2); (b) TEAH $\{(x_1) 25\text{ }^\circ\text{C}$ (\circ) +, or $(x_1) 30\text{ }^\circ\text{C}$ (Δ) +, or $(x_1) 35\text{ }^\circ\text{C}$ (\square) +, or $(x_1) 40\text{ }^\circ\text{C}$ (\bullet) +, or $(x_1) 45\text{ }^\circ\text{C}$ (\blacktriangle) +, or $(x_1) 50\text{ }^\circ\text{C}$ (\blacksquare) + DMF (x_2); and (c) TPAH $\{(x_1) 25\text{ }^\circ\text{C}$ (\circ) +, or $(x_1) 30\text{ }^\circ\text{C}$ (Δ) +, or $(x_1) 35\text{ }^\circ\text{C}$ (\square) +, or $(x_1) 40\text{ }^\circ\text{C}$ (\bullet) +, or $(x_1) 45\text{ }^\circ\text{C}$ (\blacktriangle) +, or $(x_1) 50\text{ }^\circ\text{C}$ (\blacksquare) + DMF (x_2)} at various compositions and at atmospheric pressure. Solid (—) lines correlated by the Redlich–Kister equation.

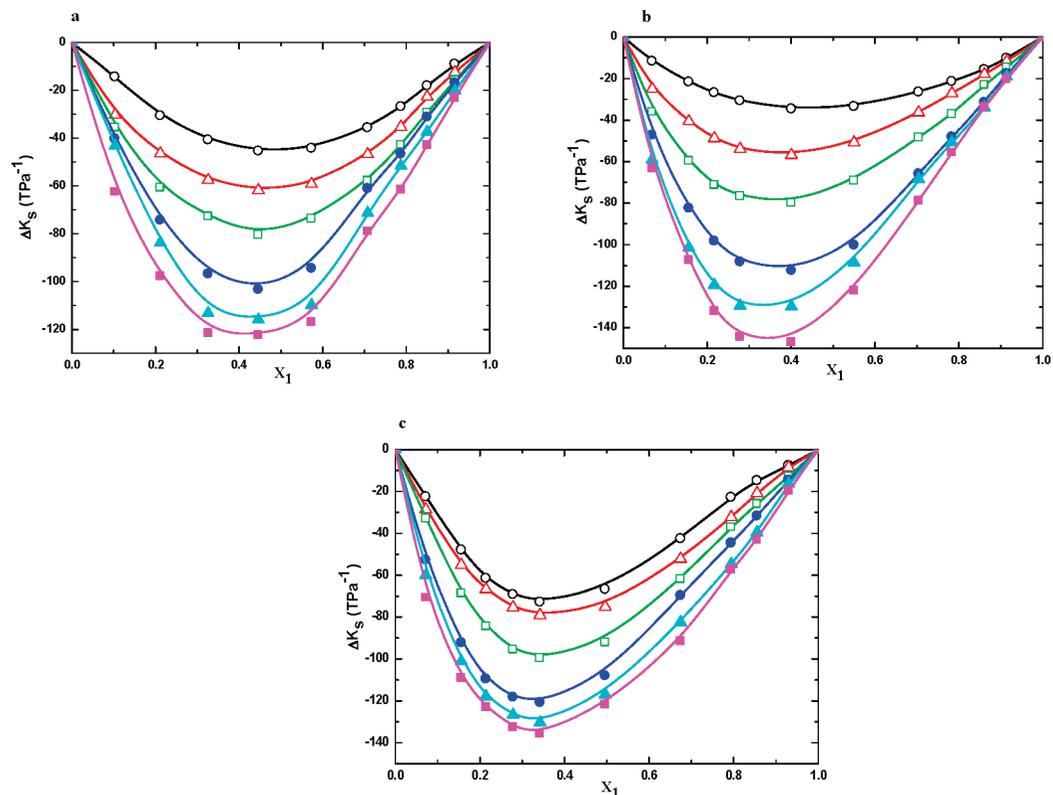
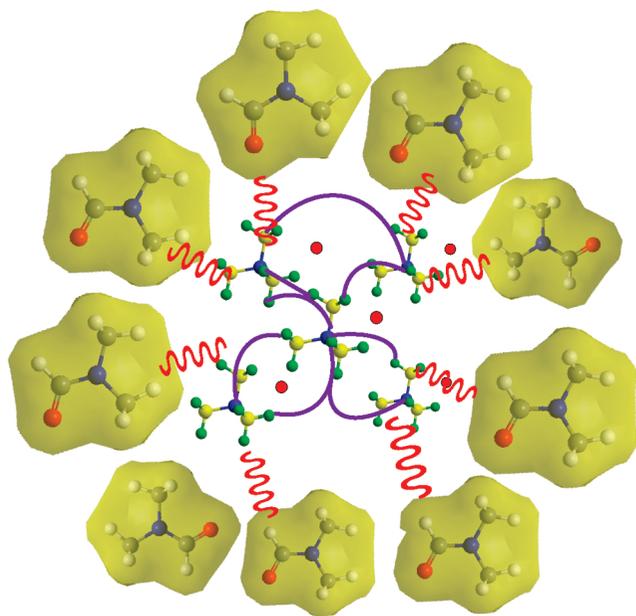


Figure 6. Deviation in isentropic compressibilities (ΔK_s) against the mole fraction of ILs (a) TMAH $\{(x_1) 25\text{ }^\circ\text{C}$ (\circ) +, or $(x_1) 30\text{ }^\circ\text{C}$ (Δ) +, or $(x_1) 35\text{ }^\circ\text{C}$ (\square) +, or $(x_1) 40\text{ }^\circ\text{C}$ (\bullet) +, or $(x_1) 45\text{ }^\circ\text{C}$ (\blacktriangle) +, or $(x_1) 50\text{ }^\circ\text{C}$ (\blacksquare) + DMF (x_2); (b) TEAH $\{(x_1) 25\text{ }^\circ\text{C}$ (\circ) +, or $(x_1) 30\text{ }^\circ\text{C}$ (Δ) +, or $(x_1) 35\text{ }^\circ\text{C}$ (\square) +, or $(x_1) 40\text{ }^\circ\text{C}$ (\bullet) +, or $(x_1) 45\text{ }^\circ\text{C}$ (\blacktriangle) +, or $(x_1) 50\text{ }^\circ\text{C}$ (\blacksquare) + DMF (x_2); and (c) TPAH $\{(x_1) 25\text{ }^\circ\text{C}$ (\circ) +, or $(x_1) 30\text{ }^\circ\text{C}$ (Δ) +, or $(x_1) 35\text{ }^\circ\text{C}$ (\square) +, or $(x_1) 40\text{ }^\circ\text{C}$ (\bullet) +, or $(x_1) 45\text{ }^\circ\text{C}$ (\blacktriangle) +, or $(x_1) 50\text{ }^\circ\text{C}$ (\blacksquare) + DMF (x_2)} at various compositions and at atmospheric pressure. Solid (—) lines correlated by the Redlich–Kister equation.

SCHEME 1: Schematic Depiction of Interactions between ILs + DMF at Various Temperatures for Positive Deviation^a

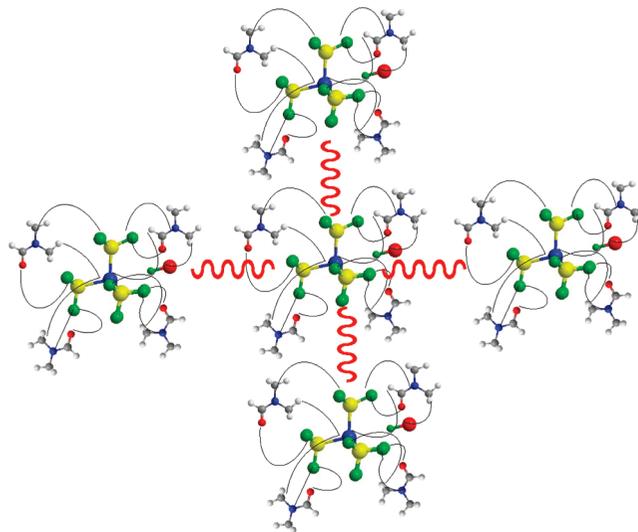


^a Color representation is as follows: green = carbon, white = hydrogen, red = oxygen, and blue = nitrogen.

between IL and DMF contributes to positive deviation. For this behavior our assumption is that at a higher concentration of IL some extensive self-association through hydrogen bonding or ion–ion interaction might be occurring. This information is represented in Scheme 1.

As seen from the experimental results in Figure 5b, in the values of V^E for DMF with TEAH there is inversion in the sign of V^E from negative to positive deviation at all temperatures except at 45 and 50 °C. The negative V^E values are observed over the entire mole fraction range at these two temperatures. The negative V^E values reveal that a more efficient packing or attractive interaction occurred when the TEAH and DMF were mixed at higher temperatures. DMF (oxygen ion of resonating structure of DMF) forms a hydrogen bond with the alkyl chain cation, while the other part of the DMF resonating structure (non-hydrogen bonding) interacts more strongly with the hydroxide ion of TEAH at higher temperatures. These interactions are shown in Scheme 2. The interactions between the DMF molecules and the alkyl chain or ions of this IL are due to ion–dipole interactions. This will reduce the hydrogen bonding between the cation and anion in the ionic liquid, which contributes to the negative V^E values. Figure 5c depicts that, at lower temperatures (25 and 30 °C), the V^E values for the system TPAH with DMF exhibit an inversion in the sign from negative to positive deviation, indicating that the interaction between TPAH and DMF decreases as the concentration of IL increases at these lower temperatures. Further, Figure 5c also shows the variation of V^E as function of mole fraction of TPAH at 35–50 °C. It can be seen that the excess volumes are negative in all range of compositions at 35–50 °C. This might be due to the large difference between molar volumes of the DMF and TPAH implying that it is possible that the relatively small organic molecules fit into the interstices upon mixing at higher temperatures. Therefore, the filling effect of organic molecular liquids in the interstices of ILs, and the ion–dipole interactions between organic molecular liquid and alkyl cation of ammonium ILs, all contribute to the negative values of V^E .

SCHEME 2: Schematic Depiction of Interactions between ILs + DMF at Various Temperatures for Negative Deviation^a



^a Color representation is as follows: green = carbon, white = hydrogen, red = oxygen, and blue = nitrogen.

It is interesting to note that the V^E values in TEAP + DMF mixture show more negative values of V^E at the DMF-rich composition than the TMAH + DMF and TPAH + DMF mixtures at 25 °C (Figure 7a), implying that in the TEAP there are ion–dipole interactions and packing effects with DMF that are stronger than those in the TMAH and TPAH solution at $x_1 \approx 0.2000$. A comparison between the positive deviation of excess volumes of TMAH + DMF with TEAH + DMF and TPAH + DMF suggests that there is a difference of the alkyl chain in all ILs, leading to variation in the hydrogen bond between the cation and anion. These results explicitly show that TMAH does not interact with DMF strongly as compared to the rest of the ILs. Furthermore, the observed positive values at IL-rich compositions show that there exists no specific interactions between unlike molecules and also that the compact structure of the polar component (DMF) due to dipolar association has been broken by these ILs. The magnitude and sign of V^E values are a reflection of the type of interactions taking place in the mixture, which are the result of different effects containing the loss of the DMF dipole interaction from each other (positive V^E) and the breakdown of the ionic liquid ion pair (positive V^E). The interaction between the ion pair of ILs increases as compared to IL + DMF interactions, which leads to positive contribution at higher IL concentration. This phenomenon is explicitly explained in Scheme 1.

It is noteworthy to compare the negative deviations of excess volumes of TMAH + DMF with those of TEAH + DMF and TPAH + DMF, suggesting that there is a difference of the alkyl chain in all ILs, leading to variation in the hydrogen bond between the cation and anion. These results explicitly demonstrate that higher alkyl chain molecules interact favorably with DMF as compared to small alkyl chain molecules, even though TEAH + DMF have more negative deviation as compared to TPAH + DMF. We might expect moderate steric hindrance of the alkyl chain in TPAH molecules.

Figure 6 illustrates the deviation in isentropic compressibility (ΔK_s) values over the whole composition range at various temperatures, for all investigated systems as a function of ILs concentration. In Figure 6, the ΔK_s values are negative over the entire composition range and at all the temperatures studied

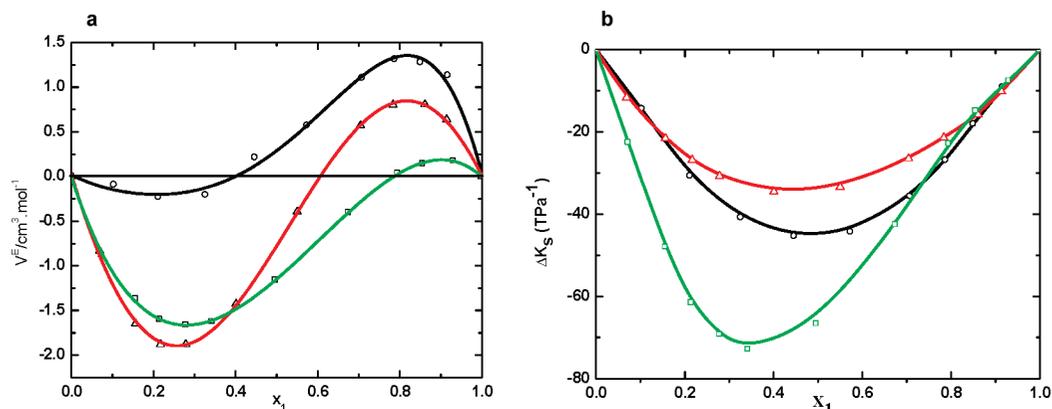


Figure 7. (a) Excess molar volumes (V^E) against the mole fraction of ILs for TMAH (○), TEAH (△), and TPAH (□) at 25 °C. (b) Deviation in isentropic compressibilities (ΔK_s) against the mole fraction of ILs for TMAH (○), TEAH (△), and TPAH (□) at 25 °C.

and approach the minimum at $x_1 \approx 0.4200$, 0.3800 , and ≈ 0.3000 for the systems TMAH with DMF, TEAH with DMF, and TPAH with DMF, respectively. As the concentrations of the ILs increase and large portions of the DMF molecules are solvated, the amount of bulk solvent decreases causing a decrease in the compressibility. The negative ΔK_s of ILs in DMF also attributed to the strong attractive interactions due to the solvation of the ions in these solvents. The negative values of the ΔK_s of the ILs with DMF imply that solvent molecules around the solute are less compressible than the solvent molecules in the bulk solutions and also negative ΔK_s values for ILs in DMF. As the mole fraction increases, the negative deviation increases sharply up to $x_1 \approx 0.4000$, while on further addition of the ILs there is decrease in the compressibility graph at all temperature ranges. This might be due to decrease in attraction of DMF and ILs molecule in IL-rich concentration region, since the interaction between the IL and IL increases and IL and DMF decreases (Scheme 1). The negative ΔK_s values for TPAH + DMF at 25 °C are higher than those for TMAH or TEAH with DMF (Figure 7b).

Recycling of Ionic Liquids. A major concern in the use of ILs is their relatively high cost, which makes their recycling an important issue for further study.^{30–32} To solve this problem herein, we have chosen a low cost and simple synthesis of ammonium ILs and eventually recycled and reused the ILs. Since large amounts of ILs were used in the various measurements, their recovery and reuse should be possible. In this case, the recovery of the ILs from binary mixture (ILs + DMF) was realized by removal of the DMF component by vacuum. No appreciable change in the physical properties of the recovered ILs was observed. The ILs can be recovered and reused by vacuuming each binary system at least two times without loss of its purity.

Conclusion

The performed work proposes to plot the temperature effect on the molecular interaction behavior with DMF molecule. To gain some insight into the new generation of green solvents, we synthesized the hydroxide group attach alkyl chain ammonium ILs. Densities and ultrasonic sound velocities for three new ILs with DMF have been reported at 25–50 °C under atmospheric pressure. From these measurements, we predicted V^E and ΔK_s at each temperature as a function of IL concentration. V^E values vary from negative to positive with increase in the mole fraction of ILs. The negative excess molar volumes reveal that a more efficient packing or attractive interaction

occurred when the IL and DMF were mixed. The V^E values exhibit an inversion in the sign from negative to positive deviation which means the interaction between IL and DMF decreases as the concentration of IL increases. However, the V^E values are positive for IL-rich compositions and negative for DMF-rich compositions for the mixture of TMAH with DMF at all investigated temperatures. The decrease in the magnitude of the negative V^E values with an increase in IL composition can be attributed to the decrease of hydrogen bonding. Although it can also be understood as an increase in the concentration of the IL, a decrease of packing efficiency between IL and DMF contributes to positive deviation. Excess properties were then fitted to the Redlich–Kister polynomial equation.

The ΔK_s values are negative over the entire composition range and at all the temperatures studied and approach the minimum at $x_1 \approx 0.4200$, 0.3800 , and ≈ 0.3000 for the systems TMAH with DMF, TEAH with DMF, and TPAH with DMF, respectively. The negative ΔK_s 's of ILs in DMF also attributed to the strong attractive interactions due to the solvation of the ions in these solvents. We are the first to show the utility of hydroxide ammonium ILs and encourage others to explore this field also. These have some additional character compared to the organic solvents in that they are reusable least two times without loss in purity.

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