Measurements and Molecular Interactions for *N*,*N*-Dimethylformamide with Ionic Liquid Mixed Solvents

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To understand the molecular interactions between *N*,*N*-dimethylformamide (DMF) with two families of ionic liquids (ILs), we have measured thermophysical properties such as densities (ρ) and ultrasonic sound velocities (u) over the whole composition range at 25 °C under atmospheric pressure. The excess molar volume (V^E) and the deviation in isentropic compressibilities (ΔK_s) were predicted using these properties 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 two families of ILs such as ammonium salts and imidazolium salts. Diethylammonium acetate ($[Et_2NH][CH_3COO]$, DEAA), triethylammonium actetate ($[Et_3NH][CH_3COO]$, TEAA), triethylammonium dihydogen phosphate ($[Et_3NH][H_2PO_4]$, TEAP), and triethylammonium sulfate ($[Et_3NH][HSO_4]$, TEAS) are ammonium salts and 1-benzyl-3-methylimidazolium chloride ([Bmim][Cl]) belongs to the imidazolium family. 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, ion-pair interactions, and hydrogen bonding between ILs and DMF molecules and their structural factors.

Introduction

Virtually, the term ionic liquids (ILs) stands for liquids composed of anions and cations. ILs are a relatively new class of compounds that are combinations of different organic salt ions that are liquid at room temperature. Due to the ionic nature of the materials, ionic liquids have essentially negligible vapor pressure and so can be envisioned as being useful in a broad 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. To date, there are over 200 types of ILs prepared, and some of them 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 volatile organic compounds 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, large range of densities and viscosities, high potential for recycling, and highly solvating capacity for organic compounds. Their perceived status as "designer", alternative "green" solvents has contributed largely to this interest, namely, the existence of fluids with no measurable volatility that 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.[1,4,6]

However, their properties and behavior with respect to solvating ability can usually be coarse-tuned either by changing the chemical nature of the cation or that of the anion. The enhancement of their characteristics is usually achieved by slightly changing the cation's size, typically by altering the alkyl chain length of its organic residue, while preserving its chemical nature. It is clear that the availability of the experimental values of parameters has a crucial significance for finding a quantitative description or even a prediction of some properties. The ILs possess many unique properties when compared to ordinary fluids. On the other hand, their structures vary and their functions are designable. These properties make them very attractive, especially in the emerging field of green chemistry. Therefore, they become the most promising solvents.

Although the number of articles on ILs is increasing exponentially, there is still a lack of data on their thermophysical description and molecular modeling properties. Apparently, the aim is to achieve exactly the desired chemical and physical properties by a judicious combination of an anion and a cation. A small number of physicochemical data are presented in the literature, which mainly characterize ILs after synthesis work.[7−11] In this context, our aim is to study closely two key thermophysical properties, density and ultrasonic sound velocity, of the molecular interactions between ILs and polar solvents. To date, there is no systematic documentation of studies of the ammonium ILs with other organic molecular solvents. For these reasons, four ammonium ILs are synthesized in our laboratory by the simplest methods, which increase their utility. In spite of their importance and interest, accurate values for many of the fundamental physical-chemical properties of this class of ILs are either scarce or even absent. On the other hand, detailed contributions of ILs with the organic molecular liquids have been rather scarcely investigated up to now on the basis of thermophysical properties and remain to be understood.

N,*N*-Dimethylformamide (DMF) is an industrial solvent and a polar solvent used widely in a variety of industrial processes,

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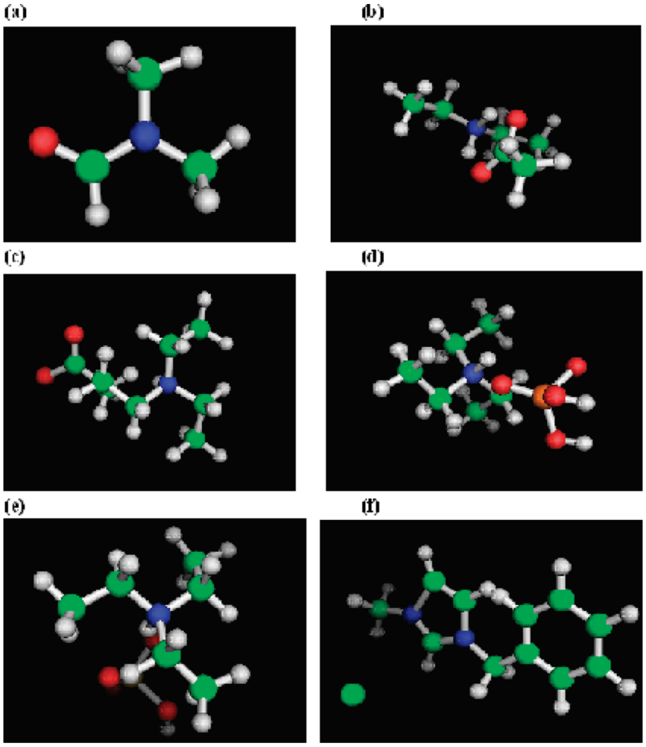
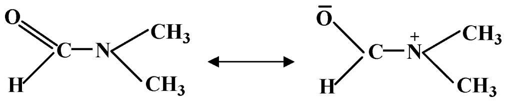


Figure 1. Schematic structures for (a) DMF, (b) DEAA, (c) TEAA, (d) TEAP, (e) TEAS, and (f) [Bmim][Cl]. Colors: green = carbon, white = hydrogen, red = oxygen, and orange = phosphorus.

among them the manufacture of synthetic fibers, leathers, films, and surface coatings.[12−14] DMF is a stable compound with a strong electron-pair donating and accepting ability and is widely used in settings such as solvent reactivity relationships.[15−17] DMF is of particular interest because any significant structural effects are absent due to the lack of hydrogen bonds, and therefore, it may be applied as an aprotic protophilic solvent with a large dipole moment and a high dielectric constant (μ = 3.24 D and ε = 36.71 at 25 °C)[18] 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 of peptides to obtain information on protein systems. The resonance structure of DMF is



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. Unshared pairs of electrons on these negatively charged, well exposed atoms enable strong solvation. The positive pole nitrogen atom, on the other hand, is buried within the molecule. In DMF the presence of two electrons repelling $-CH_3$ groups makes the lone pair at the nitrogen still more perceptible to donation.[19,20] Thus, it may be argued that DMF is actually the donator of nitrogen electron pairs. This fact is well-known as the transport phenomenon and thermophysical properties of mixed solvents. The schematic chemical structures of the DMF as well as ILs are shown in Figure 1.

The study of the properties and structure of complex liquid mixtures is necessary for both theoretical and practical points of view. Mixed solvents are almost ubiquitous in the industry in very different fields ranging from petrochemistry to pharmaceutical industries. Thermodynamic properties of mixed solvents provided by the intrinsic volume of the molecules have been considered to be a good measure of solute−solvent interactions. Experimental data of thermodynamic and thermophysical properties of liquids and liquid mixtures are fascinating and of great fundamental, practical importance from industrial points of view. Moreover, these properties allow one to draw information on the structure and interactions of mixed solvents. Although a qualitative connection between the macroscopic and microscopic features is feasible, quantitative conclusions are very much of interest in both academic and industrial communities.

To characterize the type and magnitude of the molecular interactions between DMF and ILs, we present here the V^E and ultrasonic studies of DMF with diethylammonium acetate (DEAA), triethylammonium actetate (TEAA), triethylammonium phosphate (TEAP), triethylammonium sulfate (TEAS), and 1-benzyl-3-methylimidazolium chloride ([Bmim][Cl]) at 25 °C and at atmospheric pressure over the full composition range. No effort appears to have been made to collect the molecular interactions between DMF and ILs in terms of V^E and ultrasonic studies. The mixtures of IL and DMF provide potential industrial applications for the utilization of both IL and DMF. Further, the study intends to draw molecular level information from the macroscopic properties on the molecular interaction between ILs and DMF.

Experimental Section

Materials and Syntheses. ***Materials.*** DMF (Aldrich, puriss >99.9%) and ionic liquids such as 1-benzyl-3-methylimidazolium chloride were purchased from Sigma Chemical Co. The fluids were degassed with ultrasound, kept out of the light 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 literature values.[18] The purities of the samples were further confirmed by GLC single sharp peaks. The rest of ILs were synthesized[21,22] in the laboratory with the preparations given below.

Synthesis of ILs. The ammonium family of ILs used in this work, namely, TEAA, TEAP, TEAS, and DEAA, of general type [amine][anion], were synthesized in the following way.

Synthesis of Triethylammonium Actetate (TEAA). The synthesis of ionic liquids was carried out in a 250 mL round-bottomed flask, which was immersed in a water-bath and fitted with a reflux condenser. Acetic acid (1 mol) was dropped into the triethylamine (1 mol) at 70 °C for 1 h. The reaction mixture was heated at 80 °C with stirring for 2 h to ensure that the reaction had proceeded to completion. The reaction mixture was then dried at 80 °C until the weight of the residue remained constant. The sample was analyzed by Karl Fisher titration and revealed very low levels of water (below 70 ppm). The yield of TEAA was 98%. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.778 (t, 9H), 1.466 (s, 3H), 2.58 (m, 6H), 11.0 (s, 1H).

Synthesis of Triethylammonium Phosphate (TEAP). A procedure similar to that above for TEAA was followed with the exception of the use of phosphoric acid ([anion]) instead of acetic acid. The yield of TEAP was 198 g. ^{1}H NMR (DMSO-d_6): δ (ppm) 1.18 (t, 9H), 3.06 (m, 6H), 6.37 (s, 1H). Melting point: 92 °C.

Synthesis of Triethylammonium Sulfate (TEAS). A procedure similar to that above for TEAA was followed with the exception of the use of sulfuric acid ([anion]) instead of acetic

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 25 °C and at Atmospheric Pressure

x_1	ρ/g cm^{-3}	u_{12}/m s^{-1}	V^E/cm^{-3} mol^{-1}	K_s/TPa^{-1}	ΔK_s/TPa^{-1}	x_1	ρ/g cm^{-3}	u_{12}/m s^{-1}	V^E/cm^{-3} mol^{-1}	K_s/TPa^{-1}	ΔK_s/TPa^{-1}
DEAA with DMF											
0	0.94389	1456	0	499	0	0.5400	1.01106	1517	−1.628	429	−4.5
0.0230	0.95239	1464	−0.417	489	−7.2	0.5930	1.01491	1520	−1.693	426	−1.1
0.1080	0.96984	1490	−1.066	469	−17.0	0.6600	1.01927	1523	−1.749	422	3.3
0.1390	0.97425	1487	−1.169	464	−18.5	0.7418	1.02378	1534	−1.766	415	5.8
0.1740	0.97866	1491	−1.253	460	−18.7	0.8310	1.02745	1551	−1.682	404	6.0
0.2430	0.98692	1496	−1.423	452	−17.5	0.9140	1.02766	1577	−1.251	391	2.8
0.3320	0.99519	1503	−1.504	444	−14.6	0.9590	1.02401	1595	−0.555	384	1.0
0.4580	1.00533	1512	−1.591	435	−8.7	1	1.02146	1609	0	378	0
TEAA with DMF											
0	0.94389	1456	0	499	0	0.6600	0.98890	1769	1.686	323	−38.6
0.1080	0.95665	1491	0.184	470	−6.8	0.7142	0.99224	1789	1.645	315	−35.4
0.1390	0.95949	1502	0.256	462	−8.7	0.8142	0.99957	1808	1.322	306	−23.3
0.1720	0.96211	1514	0.354	453	−10.6	0.8628	1.00427	1812	0.954	303	−16.0
0.3271	0.97290	1586	0.779	408	−22.8	0.9020	1.00823	1814	0.608	301	−9.7
0.4076	0.97715	1630	1.039	385	−29.5	0.9600	1.01300	1827	0.222	296	−3.2
0.4612	0.97920	1661	1.272	370	−33.0	1	1.01586	1840	0	291	0
0.5900	0.98538	1734	1.591	337	−39.0						
TEAP with DMF											
0	0.94389	1456	0	499	0	0.4870	1.07947	1537	−1.299	392	1.4
0.0210	0.96342	1457	−0.872	488	−6.4	0.5601	1.08783	1535	−1.060	390	15.5
0.0513	0.97935	1464	−1.270	476	−11.6	0.6301	1.09543	1531	−0.886	389	30.4
0.0960	1.00005	1471	−1.770	462	−16.4	0.7110	1.10321	1534	−0.670	385	44.7
0.1240	1.01019	1479	−1.920	452	−19.8	0.7930	1.11046	1553	−0.481	373	51.2
0.1540	1.01994	1487	−2.039	443	−22.0	0.8900	1.11813	1610	−0.263	345	44.2
0.2171	1.03642	1503	−2.091	427	−24.3	0.9544	1.12283	1699	−0.132	308	22.2
0.2981	1.05267	1521	−1.950	411	−22.2	1	1.12570	1794	0	276	0
0.3942	1.06742	1536	−1.620	397	−14.4						
TEAS with DMF											
0	0.94389	1456	0	499	0	0.5300	1.06847	1662	2.172	335	−33.6
0.0717	0.97063	1455	0.265	490	7.9	0.5600	1.07534	1694	1.949	320	−41.3
0.1410	0.98902	1456	0.803	481	16.3	0.5910	1.08195	1728	1.743	306	−48.2
0.1740	0.99553	1448	1.180	477	20.3	0.6620	1.09580	1801	1.315	279	−56.8
0.2204	1.00429	1453	1.673	469	23.4	0.8160	1.12021	1868	0.627	258	−40.3
0.2656	1.01301	1465	2.051	457	22.8	0.9030	1.13175	1853	0.298	260	−16.5
0.3300	1.02552	1488	2.443	436	17.4	0.9600	1.13867	1855	0.088	259	−4.1
0.4065	1.04167	1538	2.555	401	1.9	1	1.14289	1874	0	253	0
0.4822	1.05837	1613	2.357	360	−20.8						
[Bmin][Cl] with DMF											
0	0.94389	1456	0	499	0	0.5900	1.07799	1833	0.812	276	−47.3
0.0121	0.95449	1465	−0.456	488	−8.0	0.6580	1.08030	1873	1.734	264	−39.1
0.0247	0.96095	1472	−0.614	480	−12.0	0.7150	1.08302	1905	2.390	254	−31.5
0.1070	0.99125	1515	−0.893	439	−28.1	0.8120	1.08804	1952	3.397	241	−15.7
0.1380	1.00148	1529	−0.989	427	−31.6	0.8361	1.09005	1967	3.535	237	−12.6
0.1700	1.01067	1549	−1.017	412	−36.5	0.8555	1.09247	1978	3.532	234	−9.9
0.3240	1.04458	1646	−0.738	353	−49.6	0.8741	1.09542	1992	3.440	230	−8.4
0.4160	1.05948	1715	−0.390	321	−54.4	0.9024	1.09995	2013	3.279	224	−5.7
0.4540	1.06491	1742	−0.230	309	−54.6	0.9428	1.11019	2051	2.505	214	−3.7
0.4779	1.06805	1760	−0.116	302	−54.5	0.9590	1.11501	2062	2.085	211	−2.0
0.5062	1.07114	1778	0.072	295	−53.2	0.9737	1.11983	2077	1.638	207	−1.6
0.5442	1.07516	1805	0.317	285	−51.4	1	1.13450	2096	0	201	0

acid. The yield of TEAP was 198 g. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.3 (t, 9H), 3.16 (m, 6H), 5.04 (s, 1H). Melting point: 90 °C.

Synthesis of Diethylammonium Acetate (DEAA). A procedure similar to that above for TEAA was followed with the exception of the use of diethylamine ([amine]) instead of triethylamine. The yield of DEAA was 118 g. ^{1}H NMR ($CDCl_3$): δ (ppm) 1.3 (t, 6H), 1.97 (s, 3H), 2.95 (m, 3H), 9.20 (s, 2H).

Methods. The excess molar volumes (± 0.003 cm^3 mol^{-1}) were deduced from the densities of the pure liquids and mixtures. 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 a temperature accuracy of ±0.03 °C. Typically, density precisions are 0.000 05 g cm^{-3}. Proper calibration at each temperature is achieved with doubly distilled, deionized water and air as standards. 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 25 °C. A thermostatically controlled, well-stirred circulated water bath with a temperature controlled to ±0.01 °C was used for all the ultrasonic sound velocity measurements. The sound velocities are uncertain to 0.02%. ^{1}H (300 MHz) spectra were recorded on a Bruker 300 NMR spectrometer in $CDCl_3$ and DMSO-d_6 (with TMS for ^{1}H as internal references). The reactions were monitored by thin layer chromatography (TLC) using aluminum sheets with silica gel 60 F254 (Merck). Clear solutions were prepared by gravimetrically using a Mettler Toledo apparatus with a precision of ±0.0001 g. The uncertainty

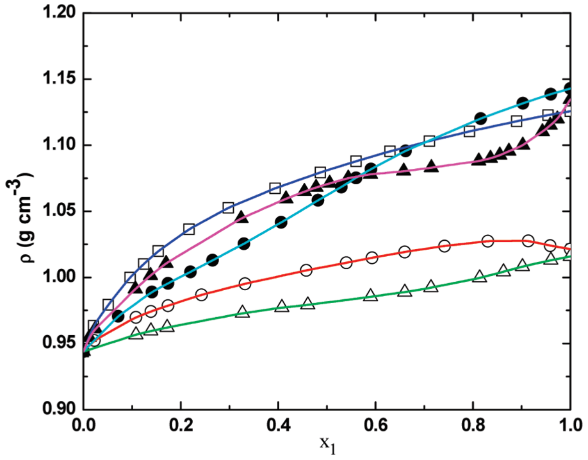


Figure 2. Densities for the mixtures of ILs with DMF vs mole fraction of IL: (○) DEAA + DMF; (△) TEAA + DMF; (□) TEAP + DMF; (●) TEAS + DMF; (▲) [Bmin][Cl] + DMF. Conditions: 25 °C and atmospheric pressure. The solid line represents the smoothness of these data.

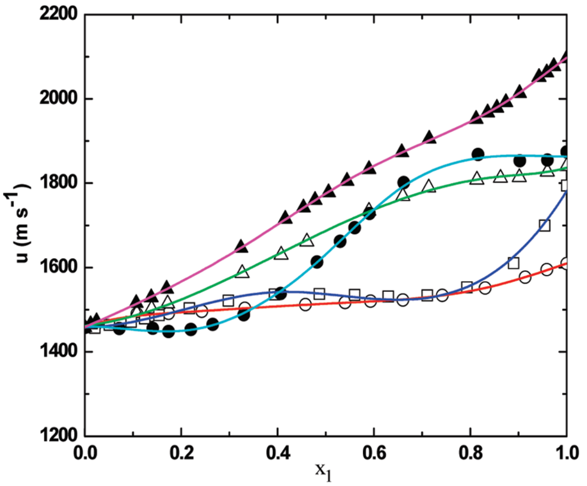


Figure 3. Ultrasonic sound velocity for the mixtures of ILs with DMF vs mole fraction of IL: (○) DEAA + DMF; (△) TEAA + DMF; (□) TEAP + DMF; (●) TEAS + DMF; (▲) [Bmin][Cl] + DMF. Conditions: 25 °C and atmospheric pressure. The solid line represents the smoothness of these data.

in solution composition expressed in mole fraction was found to be less than 5×10^{-4}.

Sample Preparation. 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 the sample was mixed, the bubble-free homogeneous sample was transferred into the u-tube of the densimeter or the sample cell of the ultrasonic interferometer through a syringe. To check whether the mixture was well homogenized, the vibrating tube was first filled with some of the contents of the syringe and a first density measurement was taken (after the temperature set point was reached). Another measurement followed when the contents of the vibrating tube were replaced with the mixture that remained in the syringe. The agreement between both values is a measure of the effectiveness of the mixing process. To guarantee the good internal consistency of the excess molar volume results, the densities of both pure components used to prepare a given mixture were also determined under experimental conditions similar to those employed during the density determination of the mixture (during the same series of density determinations, with all samples being prepared simultaneously from the same batch of pure components).

Results and Discussion

Experimental values of density and sound velocity at 25 °C are collected in Table 1 for ILs, DMF, and their mixtures over the whole composition range. Virtually, ILs are miscible with medium- to high-dielectric liquids and immiscible with low-dielectric liquids.[23] In the present study, all ILs are completely miscible in DMF ($\varepsilon = 36.71$ at 25 °C),[18] since DMF is a high dielectric liquid. The effect of the ILs on the densities and sound velocities in the DMF has been examined. It was found that the densities or sound velocities of the mixtures increase with increasing concentrations of the IL in DMF, as shown in Figure 2 or 3, respectively. The results in Figure 2 clearly show that the density values for the mixture of TEAA with DMF are lower when compared to those for the mixture of DEAA with DMF under the same experimental conditions. The density generally decreases with increasing length of an alkyl chain in a cation or anion, as was documented for ILs.[24,25] Interestingly, this conclusion is quite consistent with the observations of the present study.

Volumetric properties of binary liquid mixtures have been extensively studied, as they can contribute to clarification of the various intermolecular interactions existing between the different species found in solution and are of great importance in many fields of research as well as in industrial practice. Particularly, these properties are important for the design of industrial plants, pipelines, and pumps. Obviously, the excess volumes are determined from the densities of pure compounds (ρ_1 and ρ_2) and of mixture (ρ_m) using the standard equations.[17]

Virtually, the extent of deviation of liquid mixtures from ideal behavior is best expressed by the excess functions. Among them, the excess volumes can be interpreted in three areas, namely physical, chemical, and structural effects. The physical effects involve dispersion forces and nonspecific interactions in the mixture, adding positive contributions to V^E. The chemical and specific interactions result in a decrease in volume, which includes charge transfer type forces and other complex forming interactions between the two species; thereby these chemical effects contribute negative values to V^E. The structural effects that arise from the geometrical fitting of one component into the other are due to the different molar volumes and free volumes of pure components and add negative contributions to V^E.

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 sound velocity (u) and density (ρ)

$$K_s = u^{-2}\rho^{-1} \tag{1}$$

Deviations in isentropic compressibility (ΔK_s) were evaluated using the following relation.

$$\Delta K_s = K_s - x_1K_{s1} - x_2K_{s2} \tag{2}$$

TABLE 2: Estimated Parameters of Eq 3 and Standard Deviation, $\sigma(V^E)$, for the Systems of ILs with DMF at 25 °C

IL	a_0/cm^3 mol^{-1}	a_1/cm^3 mol^{-1}	a_3/cm^3 mol^{-1}	a_4/cm^3 mol^{-1}	a_5/cm^3 mol^{-1}	a_6/cm^3 mol^{-1}	σV^E/cm^3 mol^{-1}
DEAA	−6.3105	−1.8799	−9.4867				0.001
TEAA	5.4314	6.4860	2.6738	−4.6366	−6.3035		0.004
TEAP	−5.1521	5.8484	−4.4632	7.9908	−9.0144		0.003
TEAS	9.1937	−9.0916	−7.5877	1.2821			0.004
[Bmin][Cl]	1.0077	1.5449	2.1871	7.8281	−3.1947	2.4545	0.004

TABLE 3: Estimated Parameters of Eq 3 and Standard Deviation, $\sigma(\Delta K_s)$, for the Mixtures of ILs with DMF at 25 °C

IL	b_0/TPa^{-1}	b_1/TPa^{-1}	b_2/TPa^{-1}	b_3/TPa^{-1}	b_4/TPa^{-1}	$\sigma(\Delta K_s)$/TPa^{-1}
DEAA	−218.5	865.9	−1278.2	916.6	−285.4	2
TEAA	−93.7	412.0	−1739.2	2573.7	−1152.9	1
TEAP	−198.3	384.8	176.0	−76.2	−285.6	1
TEAS	−24.4	1957.6	−8405.6	11041.9	−4570.3	1
[Bmin][Cl]	−283.1	654.3	−1162.5	1558.3	−765.8	1

where K_{s1} and K_{s2} are the isentropic compressibilities of the pure components 1 and 2, respectively. 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:

$$Y = x_1x_2\left(\sum_{i=0}^{n} A_i(x_1 - x_2)^i\right) \tag{3}$$

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 Tables 2 and 3 along with the standard deviations of the fit. The values of V^E and ΔK_s for the binary mixtures at 25 °C as functions of ILs concentrations are included in Table 1. Figures 4 and 5 display the experimental data for the binary mixtures, and the fitted curves, along with the excess properties of the DMF with ILs as functions of IL concentrations at 25 °C.

As seen from the experimental results in Figure 4, the values of V^E for DMF with DEAA or TEAP are negative in all the ranges of composition, indicating negative deviations from ideal behavior. It is more interesting note that the V^E values in DEAA + DMF or TEAP + DMF systems have minimum values at mole fractions of this IL of about $x_1 \approx 0.75$ or $x_1 \approx 0.20$, respectively. The negative excess molar volumes reveal that a more efficient packing or attractive interaction occurred when the DEAA or TEAP and DMF were mixed. 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 acetate ion or phosphate ion of DEAA or TEAP, respectively. These interactions are shown in Scheme 1. The interactions between the DMF molecules and the alkyl chain or ions of these ILs are due to ion−dipole interactions. This will reduce the hydrogen bond between the cation and anion in the ionic liquid, which contribute to the negative V^E values. Apparently, the TEAP + DMF mixture shows more negative values of V^E at DMF-rich composition than the DEAA + DMF mixtures, implying that in the TEAP there are ion−dipole interactions and packing effects with DMF that are stronger than those in the DEAA solution. On the other hand, the DEAA + DMF mixture reveals more negative values of V^E at DEAA-rich composition than the TEAP + DMF mixture, indicating DEAA interactions and packing effects with DMF are stronger than those in the TEAP solution.

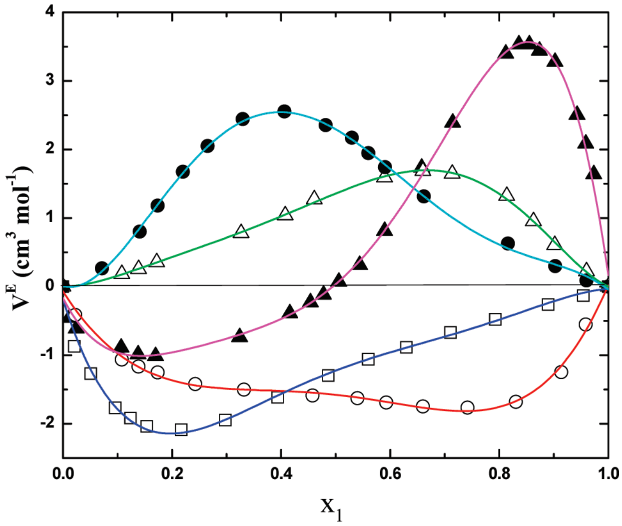


Figure 4. Excess molar volumes (V^E) against the mole fraction of ILs: (○) DEAA + DMF; (△) TEAA + DMF; (□) TEAP + DMF; (●) TEAS + DMF; (▲) [Bmin][Cl] + DMF. Conditions: 25 °C and atmospheric pressure. Solid lines are correlated by the Redlich−Kister equation.

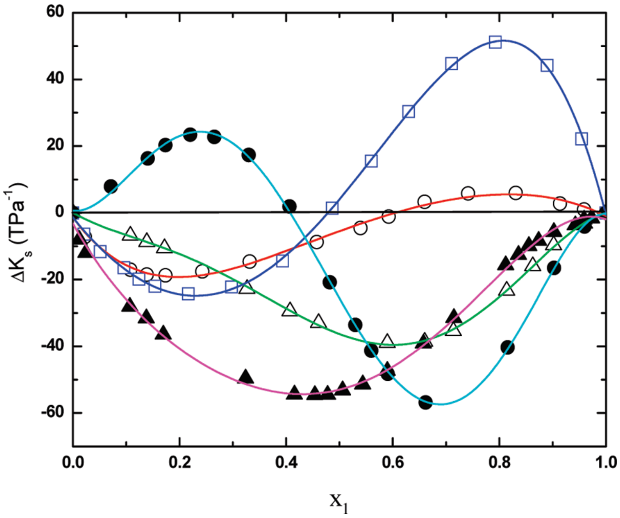
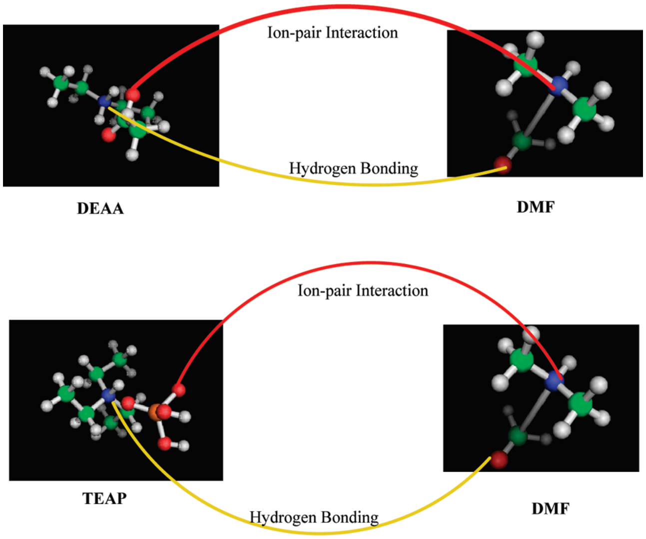


Figure 5. Deviation in isentropic compressibilities (ΔK_s) against the mole fraction of ILs: (○) DEAA + DMF; (△) TEAA + DMF; (□) TEAP + DMF; (●) TEAS + DMF; (▲) [Bmin][Cl] + DMF. Conditions: 25 °C and atmospheric pressure. Solid lines are correlated by the Redlich−Kister equation.

SCHEME 1: Interactions between TEAP + DMF and DEAA + DMF[a]

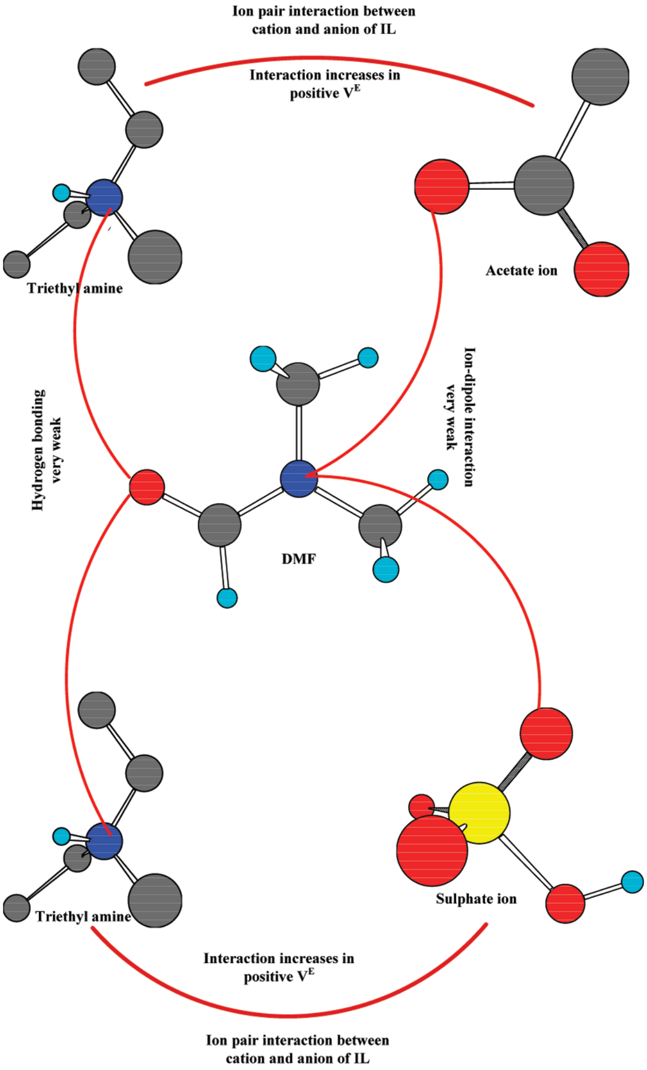


[a] Colors: green = carbon, white = hydrogen, red = oxygen, and orange = phosphorus.

As can be seen from Figure 4, the experimental results of V^E values are positive for TEAA + DMF or TEAS + DMF over the whole composition range at 25 °C. These results reveal that the factors responsible for expansion in volume are dominant over the entire composition range in the mixtures of TEAA + DMF or TEAS + DMF. Furthermore, the observed positive values show that there exist no specific interactions between unlike molecules and also 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. This phenomenon is explicitly explained in Scheme 2.

It is noteworthy to compare the excess volumes of DMF with TEAA or DEAA, which are of the same ammonium family and have the same acetate ion. A comparison between the positive excess volumes of TEAA + DMF with negative excess volumes of DEAA + DMF suggests there is a difference of the alkyl chain in both ILs, leading to variation in the hydrogen bond between the cation and anion. These results explicitly show that DEAA interacts with DMF more strongly than TEAA. We might expect moderate steric hindrance of the alkyl chain in TEAA molecules.

SCHEME 2: Interactions between TEAA + DMF and TEAS + DMF[a]

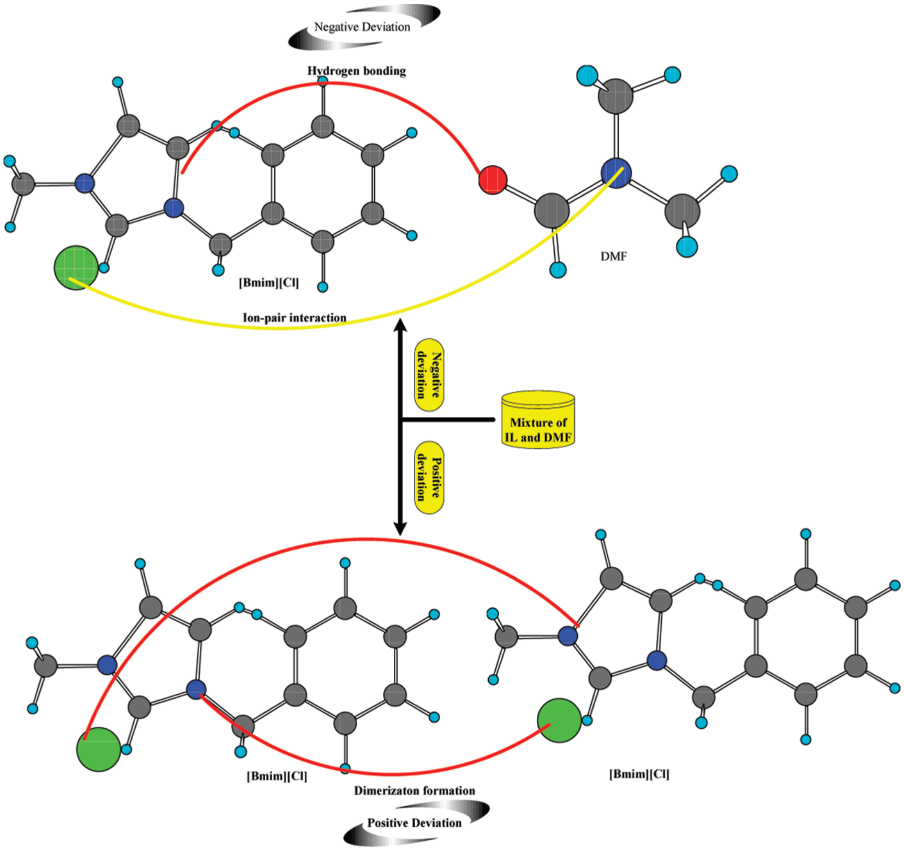


[a] Colors: blue = nitrogen, cyan = hydrogen, red = oxygen, black = carbon, and yellow = sulfur.

On the other hand, the graphical representations in Figure 4 exhibit an inversion in sign of the excess volumes in the binary mixtures of [Bmim][Cl] with DMF at 25 °C. We have observed that the excess molar volumes present a minimum at $x_1 \approx 0.17$ ($V^E = -1.017$ cm^3 mol^{-1}) and a maximum at $x_1 \approx 0.85$ ($V^E =$ 3.53 cm^3 mol^{-1}) for this system. The minimum can be due to hydrogen bonds between DMF molecules and [Bmim][Cl]. 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 [Bmim][Cl] is because it belongs to the imidazolium family. The V^E values clearly reveal that an inversion in the sign from negative to positive deviation means the interaction between [Bmim][Cl] and DMF decreases as the concentration of IL increases. Further, the V^E values are positive for IL-rich compositions and negative for DMF-rich compositions. 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 [Bmim][Cl], a decrease of packing efficiency between [Bmim][Cl] and DMF contributes to positive deviation. For this behavior our assumption is that at a higher concentration of [Bmim][Cl] some extensive self-association through hydrogen bonding or ion−ion interaction might be occurring. This information is represented in Scheme 3.

Figure 5 illustrates the deviation in isentropic compressibility (ΔK_s) values over the whole composition range at 25 °C for all investigated systems as a function of IL concentration. It is clear that different phenomena of ΔK_s were observed for the various ILs with DMF. In Figure 5, the ΔK_s values are negative over the whole composition range and approach the minimum at $x_1 \approx 0.41-0.48$ and at $x_1 \approx 0.60$ for the systems [Bmim][Cl] with DMF and TEAA with DMF, respectively. The negative values of the ΔK_s of the [Bmim][Cl] or TEAA 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 [Bmim][Cl] or TEAA in DMF. An inversion in

SCHEME 3: Interactions between [Bmim][Cl] + DMF[a]



[a] Colors: blue = nitrogen, cyan = hydrogen, red = oxygen, black = carbon, and green = chloride ion.

the sign of ΔK_s from negative to positive is observed in the mixtures of DEAA + DMF or TEAP + DMF at 25 °C. ΔK_s is negative for these mixtures rich in DMF and becomes positive with an increase in the concentration of ILs. On the other hand, an inversion in the sign ΔK_s from positive to negative is observed for the mixture of TEAS with DMF at 25 °C. ΔK_s is positive for this mixture rich in DMF and becomes negative with an increase in the concentration of TEAS. We have found that ΔK_s presents a minimum at $x_1 \approx 0.17$, 0.21, and 0.65 and a maximum at $x_1 \approx 0.83$, 0.80, and 0.22 for DEAA + DMF, TEAP + DMF, and TEAS + DMF, respectively.

Recycling of Ionic Liquids

Many researchers have pointed out the major concern in the use of ILs is their relatively high cost, which makes their recycling an important issue for further study.[22,26,27] To solve this problem herein, we have chosen the low cost and simple synthesis of ammonium ILs; eventually we recycled and reused the ILs. As a large amount of ILs were used in the measurements, their recovery and reuse should be possible. In this case, IL recovery from the binary mixture ILs + DMF was realized by removal of the DMF components by the vacuum. Appreciable changes in the physical properties of the recovered ILs have not been observed. The ammonium ILs can been recovered and reused by vacuuming each binary system at least four times without a loss in purity.

Conclusion

The work performed intends to map the thermophysical behavior of two important families of ILs, mainly imidazolium and ammonium ILs. We have considered the four ILs from ammonium families; some of them have the same cation even though with the change in anion the thermophysical properties change (e.g., TEAP shows the negative V^E values whereas TEAA and TEAS have positive V^E values with DMF). This leads to the conclusion that, herein, the alkyl chain effect of the cation is very mild but plays a major role in the interactions of ILs with DMF. The interaction between the DMF molecules and the alkyl chain of TEAP is due to ion−dipole interactions. This will reduce the hydrogen bond between the cation and anion in the IL, leading to negative V^E values, hence resulting in higher mobility of the ions, while TEAS and TEAA show positive V^E, since ion−dipole interactions of the DMF molecules and alkyl chain cations are not as strong compared to the attraction of cation and anion in ILs. On the other hand, TEAA and DEAA ILs have the same anion, while their V^E values are different; this trend is precisely illustrated by the effect of an increase in cation size and steric hindrance of the alkyl chain in TEAA molecules. These results explicitly show that DEAA interacts more strongly with DMF than TEAA. In the case of the imidazolium family, 1-benzyl-3-methylimidazolium chloride ([Bmim][Cl]) shows both positive and negative V^E values at 25 °C. Further, our results reveal that the packing efficiency between [Bmim][Cl] and DMF decreases at higher concentrations of [Bmim][Cl], contributing to positive deviation, whereas at low concentrations the packing efficiency increases, leading to negative deviation.

The values of ΔK_s also demonstrate the dominant contributions for understanding the behavior of ILs. ΔK_s's for DEAA and TEAP in DMF have negative and positive values. At low DEAA and TEAP concentrations, they have negative values. However, at high DEAA and TEAP concentrations, they have positive values. The negative ΔK_s values of [Bmim][Cl] and TEAA imply that solvent molecules around the solute are less compressible than solvent molecules in the bulk solutions; in addition, negative ΔK_s's for [Bmim][Cl] and TEAA in DMF are attributed to the strong attractive interactions due to the solvation of the ions in these solvents. However, in the case of TEAS, as the concentration of the IL increases and a large portion of the solvent molecules is solvated, the amount of bulk solvent decreases the compressibility, leading to complete negative behavior. We are the first to show the utility of simple 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 four times without loss in purity.

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