Volumetric Properties of Binary Mixtures of 1-Butyl-3-methylimidazolium Chloride + Water or Hydrophilic Solvents at Different Temperatures

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Densities for binary mixtures consisting of 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and water or hydrophilic organic solvents (methanol, acetonitrile, and *N*,*N*-dimethylformamide) have been determined at different temperatures ranging from (293.15 to 318.15) K and atmospheric pressure, with mole fractions of [bmim]Cl in the mixtures ranging from 0 to about 0.5. The density values increase as the [bmim]Cl concentration increases or the temperature decreases, and the temperature dependence has been correlated by a second-order polynomial equation. The isobaric expansivity and apparent molar volume values for these binary mixtures have been calculated from the density data. A comparison has been made for the obtained properties with those of similar systems reported in the literature when available.

Introduction

Ionic liquids (ILs) have attracted much attention from both academic and industrial scientists in the past decade and have been used in various chemical applications because of their unique characteristics such as negligible vapor pressure, high thermal and chemical stability, and the feasibility of structural and functional tunability.[1] Among the diverse varieties of ILs, chloride anion-based ILs often have relatively high hydrogen-bond basicities compared to many other ILs[2] and therefore have exhibited quite a satisfactory effect in a lot of processes involving hydrogen-bonding interactions, such as cellulose dissolution,[3] phenolic acidic compound extraction,[4] azeotropic mixture separation,[5] removal of neutral nitrogen compounds from diesel,[6] and so on. However, the chloride anion-based ILs are often extraordinarily viscous or even solid near room temperature (e.g., 1-butyl-3-methylimidazolium chloride, [bmim]Cl),[7] therefore limiting their applications in separation, dissolution, and reaction. Using the mixtures of an IL and traditional molecular solvents instead of pure ILs may be a prospective approach to this problem. The addition of solvents can significantly reduce the viscosity of the IL phase,[8] thus improving the mixing and transport behavior in the IL-involved multiphase processes. Moreover, the chemical properties such as hydrophobicity and hydrogen bond acidity and basicity of the IL phase can also be adjusted by the addition of solvents.[9]

To promote the applications of mixtures of chloride anion-based ILs and molecular solvents, the thermodynamic properties of these mixtures are needed, including volumetric properties. The volumetric properties refer to the density and other volume-related properties, which are not only informative in the understanding of IL−solvent interactions from a theoretical standpoint but also significant in the design and control of practical processes. In the past few years, the volumetric property studies have been reported for many mixtures of ILs and traditional molecular solvents, including systems involving chloride anion-based ILs.[8,10−13] However, most of these studies focused on the aqueous solution of the 1-alkyl-3-methylimidazolium chloride IL, while others studied alcoholic solutions, and the experimental data of these studies were often determined at dilute concentrations. Therefore, more studies are required to meet the practical need. On the basis of this consideration, in this work, the experimental measurements of density of the binary mixtures of [bmim]Cl + water or three hydrophilic organic solvents (methanol, acetonitrile, and *N*,*N*-dimethylformamide) were reported at different temperatures and a relatively wide concentration range, and the isobaric expansivity and apparent molar volume values were calculated on the basis of the density data.

Experimental Section

Materials. The IL [bmim]Cl was synthesized and purified according to the previous literature.[14,15] Briefly, *N*-methylimidazole was reacted with excess 1-chlorobutane at 343.15 K for 72 h. Then, the resulting mixture was washed with ethyl acetate repeatedly and dried in a vacuum line at 343.15 K for 48 h. The product was a viscous liquid and might solidify after several hours. The product was then detected by thin-layer chromatography and silver nitrate titration. In the thin-layer chromatography detection (silica gel sheet, chloroform/10 % methanol as eluent), no remaining *N*-methylimidazole or other notable impurity was found. Through the silver nitrate titration experiment (Volhard method), the purity of [bmim]Cl was found to be more than 99 % if there were no other interfering impurities. The ^{1}H NMR (500 MHz, D_2O, ppm) spectra of product were determined: δ 8.71 (s, 1 H), 7.47 (s, 1 H), 7.42 (s, 1 H), 4.17 (t, 2 H), 3.87 (s, 3 H), 1.82 (m, 2 H), 1.28 (m, 2 H), 0.88 (t, 3 H). The water mass fraction was 0.3 %, determined by a Karl Fischer titrator. The melting point of the product was about 344 K, determined by a differential scanning calorimeter (DSC Q200) under nitrogen atmosphere. Both the *N*-methylimidazole and the 1-chlorobutane were purchased from Jingchun Reagent Co., Ltd. (Shanghai, China). Methanol (purity ≥99.5 %) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetonitrile (purity ≥99.5 %) was purchased from Lingfeng Co., Ltd. (Shanghai, China). Both the methanol and the acetonitrile were used as received without further purification, and the water mass fractions were determined to be 0.03

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Table 1. Comparison of the Measured Densities ρ of Pure Solvents in This Work with the Literature Data at $T = 298.15$ K

component	ρ/g·cm^{-3} measured in this work	ρ/g·cm^{-3} literature
water	0.99705	0.99705[16]
methanol	0.78658	0.78637[16]
acetonitrile	0.77664	0.77649[16]
N,*N*-dimethylformamide	0.94386	0.94387[16]

% and 0.02 %, respectively. *N*,*N*-Dimethylformamide (purity ≥99.5 %) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and dried by 3 Å molecular sieves before use, and the water mass fraction was determined to be 0.02 %. High purity water was purchased from Wahaha Co., Ltd. (Hangzhou, China). The densities of these solvents were measured with the method introduced in the following paragraph, and the obtained results were compared with the data from literature (Table 1). All other chemicals were commercially available.

Apparatus and Procedure. Samples were prepared in glass vials by mass using an analytical balance (Sartorius CP225D) with a precision of $1 \cdot 10^{-5}$ g and were tightly sealed to minimize the absorption of moisture or the evaporation of solvents. The uncertainty of composition as a mole fraction was estimated to be less than $1 \cdot 10^{-4}$. The water content was taken into account in the preparation of samples, and the water content of the measured mixtures was about less than 0.2 %. Density was measured using an Anton Paar DMA 5000 oscillating U-tube densimeter at atmospheric pressure (about 101.2 kPa), calibrated by the ultrapure water and dry air. The calibration with ultrapure water was performed by the comparison of the density of the ultrapure water (supplied by the densimeter manufacturer) with the standard value of the density of water which was integrated in the densimeter by the manufacturer. The viscosity correction for density data was performed by the apparatus automatically. The uncertainty of temperature was 0.005 K, and the uncertainty of density measurements was found to be $3 \cdot 10^{-5}$ g·cm^{-3}. The inaccuracy of density values induced by the presence of water in the nonaqueous mixtures was estimated to be below 0.02 %. As [bmim]Cl was solid at the studied temperatures, densities were not measured for the mixtures with a mole fraction of [bmim]Cl more than 0.5.

Results and Discussion

Density. Density measurements were performed for four binary mixtures of [bmim]Cl and molecular solvents, [bmim]Cl + water, [bmim]Cl + methanol, [bmim]Cl + acetonitrile, and [bmim]Cl + *N*,*N*-dimethylformamide, covering a temperature range from (293.15 to 318.15) K with steps of 5 K. The measured densities of [bmim]Cl + water mixtures at $T = 298.15$ K and $T = 313.15$ K were compared with the data reported by Gómez et al.[8] at the same compositions and exhibited good agreement (Figure 1). As seen in the data presented in Table 2, the densities of mixtures increase with the increase of [bmim]Cl mole fraction in the mixture and also increase with the decrease of temperature. The effect of temperature on the density was further explored by fitting the data with an empirical equation. Because the density−temperature relationship was considered nonlinear,[17] a second-order polynomial was used to describe the temperature dependence of density as follows:

$$\rho = k_0 + k_1 T + k_2 T^2 \tag{1}$$

where T is the absolute temperature and k_0, k_1, and k_2 are the fit coefficients. The fit coefficients for each composition of mixtures are presented in Table S1 in the Supporting Information (SI). The standard deviations σ of correlations were calculated by using the following equation:

$$\sigma = [\sum_{i=1}^{n} (\rho - \rho_{\text{cal}})^2/(n - k)]^{1/2} \tag{2}$$

where ρ is the density value measured in this work, ρ_{cal} is the density value calculated by eq 1, n is the number of experimental data points, and k is the number of fit coefficients. The σ values obtained are all lower than $2.2 \cdot 10^{-5}$, which are also given in Table S1 (see the SI). It should be pointed out that although the density−temperature plots for the nonaqueous mixtures studied in this work (see the SI, Figure S1) seem linear to the eye and linear equations have also been used for the correlation of density−temperature function in some literature, we still select the second-order equation to correlate these functions. This is because the absolute values of parameter k_2 in eq 1, which indicate the degree of curvature of the density−temperature function, are not small enough to be regarded as zero, and the standard deviations of correlation with linear equation will be much larger than those with eq 1. Therefore, the second-order polynomial equation, eq 1, is preferred as an empirical description of the density−temperature function for all of the studied mixtures.

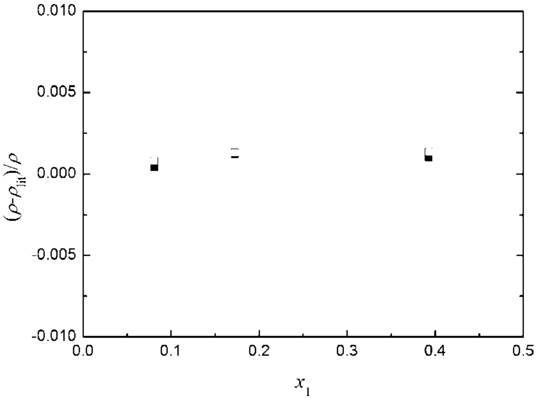

Figure 1. Deviation of experimental density (ρ) and literature density (ρ_{lit}) of the [bmim]Cl (1) + water (2) binary mixture: ■, $T = 298.15$ K; □, $T = 313.15$ K.

Isobaric Expansivity. The isobaric expansivity α is a measure of how the volume changes with temperature and is defined as:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \tag{3}$$

where subscript P indicates constant pressure. The isobaric expansivity values can be calculated by the introduction of eq 1 into eq 3, and the results are listed in Table 3. The composition of the mixture has an effect on the isobaric expansivity. In the [bmim]Cl + water mixtures, isobaric expansivity increases with the increase of [bmim]Cl concentration in the low concentration range and then reduces at higher concentrations, showing the existence of a maximum point (Figure S2 in the SI). However, in the [bmim]Cl + methanol, [bmim]Cl + acetonitrile, and [bmim]Cl + *N*,*N*-dimethylformamide mixtures, isobaric expansivity decreases with the increase of [bmim]Cl concentration over the full concentration range as shown in Figures S3, S4, and S5 in the SI. The temperature also has influence on the isobaric expansivity values. The isobaric expansivity of the mixture increases with the increase of temperature obviously in the low concentration range, but this tendency becomes not

Table 2. Experimental Density ρ of [bmim]Cl (1) + Solvent (2) from $T = 293.15$ K to $T = 318.15$ K

	ρ/g·cm^{-3}					
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
			[bmim]Cl (1) + Water (2)			
0.0000	0.99823	0.99705	0.99566	0.99404	0.99222	0.99022
0.0121	1.00706	1.00553	1.00380	1.00189	0.99981	0.99757
0.0381	1.02473	1.02246	1.02007	1.01757	1.01495	1.01224
0.0806	1.04567	1.04273	1.03973	1.03670	1.03361	1.03045
0.0819	1.04621	1.04325	1.04024	1.03717	1.03406	1.03089
0.1109	1.05573	1.05262	1.04946	1.04628	1.04306	1.03981
0.1399	1.06254	1.05939	1.05620	1.05299	1.04976	1.04648
0.1721	1.06824	1.06508	1.06190	1.05869	1.05547	1.05220
0.2489	1.07698	1.07395	1.07089	1.06782	1.06472	1.06163
0.2977	1.08014	1.07715	1.07416	1.07115	1.06814	1.06509
0.3930	1.08388	1.08100	1.07809	1.07519	1.07225	1.06937
0.4083	1.08432	1.08143	1.07853	1.07563	1.07273	1.06982
			[bmim]Cl (1) + Methanol (2)			
0.0000	0.79130	0.78658	0.78186	0.77711	0.77233	0.76752
0.0101	0.80587	0.80130	0.79671	0.79211	0.78749	0.78283
0.0506	0.85264	0.84846	0.84424	0.84001	0.83576	0.83156
0.1000	0.89410	0.89018	0.88626	0.88235	0.87844	0.87452
0.1665	0.93548	0.93183	0.92817	0.92453	0.92090	0.91727
0.1951	0.94982	0.94625	0.94269	0.93914	0.93560	0.93206
0.2398	0.96861	0.96516	0.96171	0.95826	0.95483	0.95140
0.2991	0.98902	0.98568	0.98233	0.97901	0.97569	0.97238
0.3771	1.01045	1.00723	1.00401	1.00080	0.99760	0.99441
0.4820	1.03145	1.02833	1.02522	1.02212	1.01903	1.01596
			[bmim]Cl (1) + Acetonitrile (2)			
0.0000	0.78204	0.77664	0.77121	0.76575	0.76025	0.75473
0.0303	0.81547	0.81040	0.80529	0.80018	0.79505	0.78988
0.0797	0.85907	0.85438	0.84967	0.84495	0.84021	0.83548
0.1308	0.89446	0.89007	0.88568	0.88127	0.87686	0.87245
0.1806	0.92276	0.91862	0.91446	0.91030	0.90614	0.90198
0.2350	0.94831	0.94436	0.94039	0.93647	0.93251	0.92857
0.2914	0.97009	0.96632	0.96255	0.95878	0.95502	0.95126
0.3717	0.99509	0.99152	0.98795	0.98438	0.98083	0.97728
0.4390	1.01249	1.00908	1.00566	1.00225	0.99886	0.99546
			[bmim]Cl (1) + *N*,*N*-Dimethylformamide (2)			
0.0000	0.94863	0.94386	0.93908	0.93429	0.92948	0.92468
0.0332	0.96192	0.95733	0.95273	0.94812	0.94352	0.93889
0.0835	0.97800	0.97363	0.96925	0.96487	0.96048	0.95609
0.1303	0.99054	0.98633	0.98213	0.97791	0.97371	0.96950
0.1822	1.00271	0.99867	0.99462	0.99058	0.98654	0.98251
0.2289	1.01204	1.00812	1.00421	1.00030	0.99640	0.99250
0.3069	1.02551	1.02178	1.01805	1.01434	1.01063	1.00694
0.3879	1.03710	1.03354	1.02998	1.02642	1.02289	1.01936
0.4488	1.04453	1.04106	1.03761	1.03418	1.03077	1.02736

clear and even inversed while the [bmim]Cl concentration increases.

Apparent Molar Volume. The apparent molar volume of a solute is defined as the volume, V, of a solution containing n_1 moles of solute minus the volume attributed to the n_2 moles of solvent present, considered as pure solvent of the molar volume V_2^*, per mole of solute:

$$V_\phi = (V - n_2V_2^*)/n_1 \tag{4}$$

where V is the volume of solution, V_2^* is the molar volume of pure solvent, n_1 is the number of moles of solute, and n_2 is the number of moles of solvent.[18] The apparent molar volume can be calculated from the experimental density values of solutions and pure solvents using the following equation:

$$V_\phi = \frac{M_1}{\rho} - 1000\frac{(\rho - \rho_0)}{(\rho\rho_0 m)} \tag{5}$$

where M_1 is the molecular weight of solute (in g·mol^{-1}), m is the molality of solution (in mol·kg^{-1}), and ρ and ρ_0 are the densities of the solution and the pure solvent, respectively (in g·cm^{-3}). The apparent molar volume values are listed in Table S2 in the SI, and it is found that the composition dependence of apparent molar volumes is quite different between the aqueous solution of [bmim]Cl and the other three organic solvent systems. As shown in Figure S6 in the SI, the apparent molar volume of the [bmim]Cl + water mixture decreases rapidly as the molality increases in the low molality range and then increases slowly after passing through a minimum point. This trend agrees with that reported by Gómez et al. about the same system[8] and is also observed in the binary mixtures of 1-alkyl-3-methylimidazolium bromide + water[19,20] and the aqueous solutions of tetraalkylammonium salts[21] but is different from that observed in the aqueous solutions of alkali halides.[22] On the other hand, as Figures S7, S8, and S9 in the SI show, in the organic solutions of [bmim]Cl in methanol, acetonitrile, and *N*,*N*-dimethylformamide, the apparent molar volumes keep rising over the whole concentration range measured, rapidly in the low molality range and more slowly at higher molalities. This trend is also observed in other binary mixtures of IL and organic solvents, for example, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF$_4$) or [bmim]Cl + ethanol[11,23] and 1-alkyl-3-methylimidazolium bromide + methanol or ethanol,[20,24] and is also similar to that in many other mixtures consisting of halide electrolytes with organic solvents.[25,26] As seen from Figures

Table 3. Isobaric Expansivity α of [bmim]Cl (1) + Solvent (2) from T = 293.15 K to T = 318.15 K

	$10^4\ \alpha/\mathrm{K}^{-1}$					
x_1	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15	T/K = 318.15
			[bmim]Cl (1) + Water (2)			
0.0000	2.174	2.593	3.014	3.437	3.863	4.290
0.0121	2.897	3.253	3.611	3.970	4.332	4.696
0.0381	4.334	4.562	4.791	5.022	5.255	5.489
0.0806	5.570	5.686	5.802	5.920	6.039	6.158
0.0819	5.610	5.725	5.841	5.958	6.076	6.195
0.1109	5.874	5.955	6.037	6.120	6.203	6.287
0.1399	5.909	5.981	6.054	6.127	6.201	6.276
0.1721	5.885	5.950	6.016	6.082	6.149	6.216
0.2489	5.628	5.675	5.721	5.769	5.816	5.864
0.2977	5.507	5.548	5.589	5.630	5.671	5.713
0.3930	5.342	5.364	5.387	5.409	5.432	5.455
0.4083	5.332	5.353	5.374	5.395	5.417	5.438
			[bmim]Cl (1) + Methanol (2)			
0.0000	11.86	11.99	12.13	12.27	12.41	12.55
0.0101	11.31	11.42	11.54	11.66	11.78	11.90
0.0506	9.855	9.922	9.990	10.06	10.13	10.20
0.1000	8.766	8.801	8.837	8.873	8.909	8.946
0.1665	7.829	7.843	7.857	7.871	7.885	7.899
0.1951	7.521	7.532	7.543	7.554	7.565	7.577
0.2398	7.141	7.154	7.166	7.178	7.191	7.203
0.2991	6.779	6.783	6.786	6.789	6.793	6.796
0.3771	6.391	6.396	6.400	6.404	6.408	6.412
0.4820	6.065	6.061	6.056	6.052	6.047	6.042
			[bmim]Cl (1) + Acetonitrile (2)			
0.0000	13.77	13.95	14.12	14.31	14.49	14.68
0.0303	12.42	12.55	12.68	12.82	12.95	13.09
0.0797	10.92	11.01	11.10	11.18	11.27	11.37
0.1308	9.808	9.871	9.935	9.999	10.06	10.13
0.1806	8.991	9.039	9.088	9.137	9.187	9.238
0.2350	8.343	8.371	8.399	8.428	8.456	8.485
0.2914	7.781	7.805	7.829	7.853	7.877	7.902
0.3717	7.193	7.206	7.219	7.232	7.245	7.258
0.4390	6.758	6.769	6.780	6.791	6.802	6.813
			[bmim]Cl (1) + *N*,*N*-Dimethylformamide (2)			
0.0000	10.05	10.12	10.19	10.27	10.34	10.41
0.0332	9.538	9.599	9.660	9.722	9.785	9.848
0.0835	8.936	8.987	9.037	9.089	9.141	9.193
0.1303	8.496	8.533	8.569	8.606	8.643	8.681
0.1822	8.076	8.102	8.129	8.155	8.182	8.209
0.2289	7.747	7.767	7.788	7.808	7.829	7.849
0.3069	7.293	7.300	7.307	7.314	7.321	7.328
0.3879	6.890	6.895	6.901	6.906	6.911	6.916
0.4488	6.652	6.642	6.633	6.623	6.613	6.603

S6 to S9 of the SI, the temperature dependence of the apparent molar volume is also different for the two kinds of mixtures. In the aqueous case, the apparent molar volume increases as the temperature increases, while in the nonaqueous solutions the apparent molar volume tends to decrease with the rise of temperature at an infinite concentration. The remarkable distinction of apparent molar volume behavior between aqueous and nonaqueous solutions probably resulted from the different ion−solvent interactions and the different microscopic structures in the solutions. For example, Zafarani-Moattar and Shekaari have found that the ion−water interaction was stronger than the ion−alcohol interactions for the [bmim]Br + water or methanol or ethanol solutions,[24] and Wen et al. have demonstrated the existence of a clathrate-like arrangement in the aqueous solution of tetrabutylammonium bromide which has a similar structure to [bmim]Cl.[21]

Conclusions

In this work, the density values of four binary mixtures of [bmim]Cl with water or hydrophilic organic solvents (methanol, acetonitrile, and *N*,*N*-dimethylformamide) were measured and presented from (293.15 to 318.15) K at atmospheric pressure. The density values showed clear dependence on both the composition and the temperature, and the temperature dependence was correlated by a second-order polynomial equation. The isobaric expansivity and apparent molar volume values for these binary mixtures were calculated from the density data and exhibited different behavior between the [bmim]Cl + water mixture and the other three nonaqueous mixtures. The obtained volumetric properties were compared to those of similar binary systems reported in the literature when available and exhibited good agreement.

Supporting Information Available:

Fit coefficients and standard deviations for the empirical correlation of densities as a function of temperature. Calculated apparent molar volumes of [bmim]Cl + solvent mixtures. Density for the [bmim]Cl + acetonitrile binary mixture plotted against temperature at different compositions. Isobaric expansivities and apparent molar volumes of the studied binary mixtures plotted against composition at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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