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Viscosity and Density Measurements for Six Binary Mixtures of Water (Methanol or Ethanol) with an Ionic Liquid ([BMIM][DMP] or [EMIM][DMP]) at Atmospheric Pressure in the Temperature Range of (293.15 to 333.15) K

Yin-hui Gong,[†,‡] Chong Shen,[†,‡,§] Ying-zhou Lu,[‡] Hong Meng,[‡] and Chun-xi Li*[†,‡]

[†] State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China
[‡] College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China
[§] Liming Research Institute of Chemical Industry, Luoyang, 471000, P. R. China

S *Supporting Information*

ABSTRACT: The experimental data of viscosity and density for six binary mixtures of water (methanol or ethanol) with an ionic liquid, 1-butyl-3-methylimidazolium dimethylphosphate ([BMIM][DMP]) or 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM][DMP]), were measured in the temperature range of (293.15 to 333.15) K at atmospheric pressure using a viscometer and densimeter. The solution behavior of the mixtures is discussed in terms of the variation of the excess viscosity and excess volume with temperatures and compositions. It is found that both excess volume and viscosity of the mixtures studied show a negative deviation from the ideal solution behavior, and the viscosity of the mixtures decreases drastically with the increase of temperatures and mole fractions of solvents. The excess volume of the binary mixtures is quite low, in the range of (1.0 to 1.9) $\mathrm{cm^3 \cdot mol^{-1}}$; moreover, it shows a monotonic decrease with increasing temperature for the aqueous solution of ILs and a reverse trend for the IL solutions of methanol or ethanol at any concentrations.

INTRODUCTION

Ionic liquids (ILs), as a hybrid of neutral and ionic entities, show some unique properties, like negligible volatility, good conductivity and stability, and high solvating capacity for polar and nonpolar compounds, and are deemed as a potential greener solvent for many reactions and separation processes. For example, ILs might be applicable in the extractive desulfurization of fuel oils[1,2] and in extractive distillation of some mixtures with close boiling points or azeotropes[3,4] depending on the task and specific constituents of ILs. From the application point of view, it is necessary to know the physical and thermodynamic properties of ILs and their mixtures with other solvents, for example, density and viscosity, for the process design. From the academic point of view, the physical and thermodynamic data are also crucial in understanding the structure−property relationship of ILs and the interaction between different ILs and solvents, in developing thermodynamic models,[5] and accordingly guiding the design of a task-specific ILs for different purposes.

By far, many experimental data of density and viscosity of pure ILs have been reported and documented in some recent reviews;[6,7] however, the same property data for the IL-containing mixtures are quite scarce in comparison with the huge amount of IL species and possible combination approaches with different solvents. In our group, a series of vapor−liquid equilibrium data have been measured for water−methanol−ethanol systems containing an imidazolium-based ILs with a dialkylphosphate anion, for example, [MMIM][DMP], [EMIM][DEP], [BMIM][DBP], and [EEIM][DEP],[8−10] aimed to find an appropriate entrainer for the efficient separation of ethanol−water solution. It is found that some of these ILs have a profound salting-out effect and can even break the azeotropic phenomena of the ethanol−water mixture at a specified IL-content and facilitate the distillation separation. To our understanding, these halogen-free ILs are of potential applicability and are superior to others in terms of their ease of production, cheapness, negligent corrosiveness to the steel, and miscibility to all components in the whole concentration range. In this work, we measured the viscosity and density of six binary mixtures of water (methanol or ethanol) with an IL [EMIM][DMP] or [BMIM][DMP] at atmospheric pressure in the temperature range of (293.15 to 333.15) K. The experimental data were correlated as a function of temperature and composition by two different equations, and the solution behavior of these IL-containing mixtures were discussed in terms of the variation of excess viscosity and molar volume with temperature, composition, and the characteristics of pure components.

EXPERIMENTAL SECTION

Chemicals. The chemicals used for synthesizing ILs [EMIM][DMP] and [BMIM][DMP] are 1-ethylimidazole and 1-butylimidazole (≥ 99.5 wt %, Zhejiang Kaile Reagents Company, China), trimethylphosphate (≥ 99.5 wt %, Tianjin Guangfu Reagents Company, China), and ether (≥ 99.5 wt. %, Beijing Yili Reagents Company, China), which were used as received. The solvents of methanol and ethanol were supplied by Beijing Chemical Plant with nominal purity above 99.7 wt %, and the

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Table 1. Viscosity, η (mPa·s), Data of the Pure Components at Different Temperatures in Kelvin

	viscosity at the following temperatures, T (K)								
component	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
methanol	0.568	0.532	0.501	0.473	0.448	0.426	0.406	0.387	0.371
water	1.004	0.894	0.801	0.726	0.656	0.599	0.554	0.509	0.470
ethanol	1.141	1.037	0.946	0.865	0.793	0.730	0.673	0.622	0.576
[EMIM][DMP]	378.818	269.872	198.129	149.210	114.940	90.274	72.229	58.733	48.503
[BMIM][DMP]	830[a]	584.740	409.881	293.976	216.260	162.610	124.607	97.376	77.252

[a] Obtained by extrapolation.

quality of water was Milli-Q as determined by the Karl Fisher titrator (type CBS-1A). The alcohols used were degassed ultrasonically and dried by the activated fresh molecular sieves of type 4 Å (Union Carbide). The ILs [EMIM][DMP] and [BMIM][DMP] were prepared and purified in the laboratory according to the method described in the literature,[11] and their purities in mole fraction were better than 99% as determined by the NMR analysis and verified by the elemental analysis (type vario EL, Elementar Analysensysteme GmbH, Germany) (see the Supporting Information).

Viscosity Measurement. The viscosities of pure ILs and their binary mixtures with water (methanol or ethanol) at different temperatures were measured using the AMVn automated micro viscometer (Anton Paar Co. Ltd., Austria). The binary mixtures with different mole fractions of ILs were prepared by weighing with an electronic balance (type AR 2130, Ohaus Co. Ltd., USA) with a mass precision of ± 0.001 g. The nominal uncertainty of the experimental viscosity is less than $5 \cdot 10^{-5}$ mPa·s, and the precision of the temperature is less than 0.05 K. The viscometer was calibrated by measuring the viscosity of pure water at different temperatures, and the comparative results are listed in Table S1 (see the Supporting Information), showing that the maximum uncertainty is within ± 0.005 mPa·s.

Density Measurement. Density data in the temperature range of (293.15 to 333.15) K were measured for the same samples as that for the viscosity measurement by means of the digital vibrating tube densimeter (DMA 4500M, Anton Paar Co. Ltd., Austria). The uncertainty of the density measurement is $\pm 1 \cdot 10^{-5}$ g·cm^{-3}, and the temperature precision is ± 0.01 K. The accuracy of the density data were verified by comparing the experimental data of water at different temperatures with the reference data,[12] as shown in Table S2 (see the Supporting Information), indicating that the measurement accuracy is about ± 0.0002 g·cm^{-3}.

RESULTS AND DISCUSSION

Viscosity of Pure Components. The viscosity data of pure components, namely, water, methanol, ethanol, [EMIM][DMP], and [BMIM][DMP], at atmospheric pressure were measured in the temperature range of (293.15 to 333.15) K and are presented in Table 1. As shown in Table 1, the viscosities of the ILs studied here are much higher, varying from hundreds to thousands of times, than that of the molecular solvents, and follows the order of [BMIM][DMP] > [EMIM][DMP] ≫ ethanol > water > methanol at any temperatures. The viscosity of [BMIM][DMP] at 293.15 K is too high to be measurable by the present viscometer and is estimated as 830 mPa·s by the extrapolation method using the experimental data at other temperatures and the overall variation trend of viscosity with temperature. The high viscosity of IL may be dominated by the "ionic" attributes of the liquid and the strong Coulombic interaction among different ions and ionic clusters. The migration of an IL entity, or an ionic pair, in the liquid will be strongly pulled by the surrounding ionic spheres with equal but opposite charge and thus shows a strong

Table 2. Viscosity, η (mPa·s), Data for Six Binary Mixtures at Different Temperatures and Mole Fractions of ILs

	viscosity at the following temperatures, T (K)								
x_{IL}	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
				[EMIM][DMP] + Water					
0.201	32.348	25.472	20.436	16.677	13.810	11.571	9.812	8.405	7.264
0.400	98.623	74.531	57.701	45.445	36.431	29.685	24.551	20.584	17.462
0.601	194.918	143.368	108.108	83.534	65.745	52.726	42.988	35.565	29.812
0.802	292.343	211.807	157.392	119.676	93.005	73.709	59.374	48.609	40.334
				[BMIM][DMP] + Water					
0.201	39.936	30.676	24.165	19.421	15.814	13.136	11.047	9.371	8.037
0.399	148.336	108.497	81.588	62.544	48.934	39.047	31.670	26.046	21.688
0.602	356.366	250.809	181.569	134.707	101.957	78.841	62.069	49.685	40.404
0.799	593.811	409.699	290.737	211.596	157.545	119.723	92.692	73.115	58.548
				[EMIM][DMP] + Methanol					
0.201	5.308	4.769	4.309	3.911	3.566	3.265	2.998	2.763	2.555
0.402	24.323	20.624	17.641	15.256	13.281	11.668	10.298	9.132	8.188
0.601	77.923	61.738	49.686	40.719	33.843	28.412	24.241	20.815	18.062
0.802	197.568	147.795	112.671	88.009	70.158	56.834	46.728	39.023	32.965
				[BMIM][DMP] + Methanol					
0.200	7.184	6.267	5.536	4.924	4.401	3.972	3.665	3.338	3.051
0.400	38.581	31.585	26.194	21.992	18.594	15.944	13.783	11.987	10.477
0.596	150.124	113.293	87.517	68.693	54.857	44.367	36.488	30.369	25.512
0.797	394.706	281.661	206.282	154.422	117.922	91.507	72.468	58.301	47.598
				[EMIM][DMP] + Ethanol					
0.202	6.898	6.127	5.471	4.904	4.425	4.004	3.634	3.318	3.037
0.402	27.628	23.295	19.834	17.054	14.796	12.922	11.364	10.044	8.951
0.602	87.272	68.828	55.237	44.999	37.369	31.252	26.444	22.643	19.564
0.801	190.592	142.736	109.485	85.764	68.426	55.531	45.747	38.213	32.266
				[BMIM][DMP] + Ethanol					
0.200	8.842	7.704	6.718	5.933	5.272	4.711	4.227	3.811	3.454
0.400	42.079	34.296	28.176	23.565	19.869	16.973	14.589	12.661	11.058
0.601	150.932	114.441	88.926	69.864	55.652	45.202	37.082	30.893	25.945
0.799	396.008	283.634	210.325	155.712	118.991	92.659	73.322	59.057	48.159

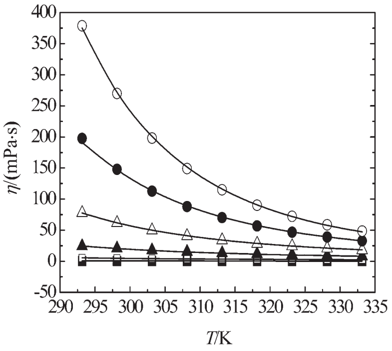

Figure 1. Experimental and correlative viscosity for the binary mixture of [EMIM][DMP] and methanol at different temperatures and mole fractions of IL: ■, 0; □, 0.201; ▲, 0.402; △, 0.601; ●, 0.802; ○, 1; —, calculated values from eq 1.

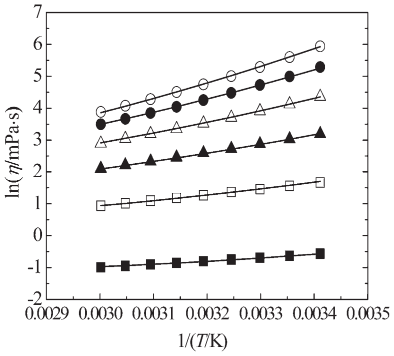

Figure 2. Plot of ln(η/mPa·s) against 1/(T/K) for the same data sets and legends as noted in Figure 1.

drag force for the movement, resulting in a high viscosity. Besides, the viscosity of the pure IL decreases drastically with the increasing temperature, for example, the viscosity of [EMIM][DMP] decreases 87 %, that is, from 378.818 mPa·s at 293.15 K to 48.503 mPa·s at 333.15 K, while the viscosity of methanol decreases least, being only 34 % in the same temperature range. Thus the viscosity of IL is more sensitive to temperature than the conventional molecular solvents.

Viscosity Correlation for the Binary Mixtures. The viscosity data for the IL-containing binary mixtures at the mole fraction of ILs, x_{IL}, being about 0.2, 0.4, 0.6, and 0.8, were measured at the same pressure and temperature as that for pure components and are presented in Table 2. To show the variation of the viscosity of a binary mixture with the IL content and temperature, the experimental data were plotted for different binary systems. It is found that all of the binary systems follow the same variation pattern. As a representative, the experimental viscosity data for the binary mixture of [EMIM][DMP] and methanol in the temperature range of (293.15 to 333.15) K are presented in Figures 1 and 2, respectively, in terms of different scales, namely, η versus T and ln(η/mPa·s) against 1/(T/K). As shown in Figure 1, the viscosity of pure IL [EMIM][DMP] at lower temperature, for example, 293.15 K, is much higher than that of methanol, and the viscosity of the binary mixture decreases drastically with the decrease of the IL content at the same temperature. For example, the viscosity varies from 378.818 mPa·s for the pure IL to 77.923 mPa·s for the binary mixture at mole fraction of IL being 0.601, indicating that the viscosity of [EMIM][DMP] can decrease about 80 % by adding only 8.3 wt % of methanol to it. The drastic decrease of viscosity of the mixture by the addition of molecular solvent like methanol may be attributed to the following facts. First, the molecular solvent has a much lower viscosity than the pure IL, which reduces the bulk viscosity of the binary mixture greatly due to the diluting effect. Second, the dielectric behavior of the solvent can reduce the Coulomb interaction between ions to only a few percent of that in a pure IL state, considering that the Coulomb interaction in a pure IL is free of dielectrics ($D = 1$), while in a binary mixture the dielectric constant (D) is quite high, ranging from 25.7 for ethanol to 78.2 for water at 293.15 K. Third, the ions are largely separated by the dissolved solvent molecules and thus reduce the Coulomb interaction and increase the fluidity of the liquid mixture.

As shown in Figure 2, at a fixed composition of the binary mixtures, the ln(η/mPa·s) values always decrease linearly with increasing temperatures, which is consistent with the Eyring kinetic equation

$$\eta = \eta_\infty \exp\left(\frac{E_a}{RT}\right) \tag{1}$$

where η_∞ is the viscosity at infinite temperature. E_a is the activation energy of the solution and is related to the temperature and composition of the binary system. Considering the good linearity of ln(η/mPa·s) against 1/(T/K) and the regular variation of viscosity with composition in the whole concentration range, the viscosity data listed in Tables 1 and 2 were correlated together with the following equations for the activation energy and η_∞.[13]

$$E_a = \sum_{i=1}^{3}\left(A_i + \frac{B_i}{T}\right)x_{\mathrm{IL}}^{i-1} \tag{2}$$

$$\eta_\infty = \sum_{i=1}^{2} C_i x_{\mathrm{IL}}^{i-1} \tag{3}$$

where x_{IL} is the mole fraction of IL. A_i, B_i, and C_i are regression parameters determined by the least-squares method. Table 3 lists the regressed parameters along with the average absolute relative deviations (ARD) between the experimental and the correlated values for each of binary systems.

Excess Viscosity. An excess property is a good indicator to reflect the deviation of a real solution to the ideal mixture. The excess viscosity of the solution, η^E, is defined by eq 4:

$$\eta^E = \eta_{\mathrm{mix}} - x_{\mathrm{IL}}\eta_{\mathrm{IL}} - x_S\eta_S \tag{4}$$

where η_{IL}, η_S, and η_{mix} refer to the viscosity of pure IL, solvent, and the binary mixture, respectively. x_{IL} and x_S refer to the mole fraction of IL and solvent, respectively. To analyze the solution behavior, the experimental excess viscosity at different temperatures and compositions were plotted for all the binary mixtures studied and found that they all follow a very similar pattern. As representative examples, Figures 3 and 4 present the plots of excess viscosity for the binary mixtures of ([BMIM][DMP] + methanol) and ([BMIM][DMP] + water), respectively. It is found that all of the binary mixtures studied here show a negative deviation from the ideal solution behavior and have a low-water mark, as indicated by the negative excess viscosities over the whole temperature and concentration ranges. The excess

Table 3. Regressed Parameters of Equations 2 and 3 along with the Deviation in ARD for the Six Binary Systems Studied

correlation results	IL + solvent binary systems		
IL = [EMIM][DMP]	IL + water	IL + methanol	IL + ethanol
A_1	$-3.8614\cdot10^4$	$-2.8576\cdot10^4$	$-2.2986\cdot10^4$
A_2	$-4.5725\cdot10^4$	$-9.3071\cdot10^3$	$3.1757\cdot10^3$
A_3	$2.7644\cdot10^4$	$-7.8919\cdot10^3$	$-1.6393\cdot10^4$
B_1	$8.6677\cdot10^6$	$5.7321\cdot10^6$	$5.6154\cdot10^6$
B_2	$1.6273\cdot10^7$	$7.1587\cdot10^6$	$3.1172\cdot10^6$
B_3	$-9.7957\cdot10^6$	$8.0633\cdot10^5$	$3.5046\cdot10^6$
C_1	43.3320	22.9690	5.4561
C_2	$2.7814\cdot10^3$	$2.3129\cdot10^2$	32.6850
ARD[a]	2.19 %	1.03 %	1.96 %
IL = [BMIM][DMP]	IL + water	IL + methanol	IL + ethanol
A_1	$-3.1454\cdot10^4$	$-3.0027\cdot10^4$	$-2.1625\cdot10^4$
A_2	$-5.5025\cdot10^4$	$-1.9675\cdot10^4$	$-6.7902\cdot10^3$
A_3	$3.3567\cdot10^4$	$-2.0837\cdot10^3$	$-1.0801\cdot10^4$
B_1	$7.5169\cdot10^6$	$5.9568\cdot10^6$	$5.4089\cdot10^6$
B_2	$1.9980\cdot10^7$	$1.1003\cdot10^7$	$6.6933\cdot10^6$
B_3	$-1.1909\cdot10^7$	$-1.2063\cdot10^6$	$1.7271\cdot10^6$
C_1	11.3950	30.4290	4.1743
C_2	$7.0156\cdot10^2$	$3.5098\cdot10^2$	28.4340
ARD	2.14 %	1.35 %	1.29 %

[a] ARD = $(1/n)\Sigma_{i=1}^{n}|\eta_{\text{cal}}/\eta_{\text{exp}} - 1.0|$.

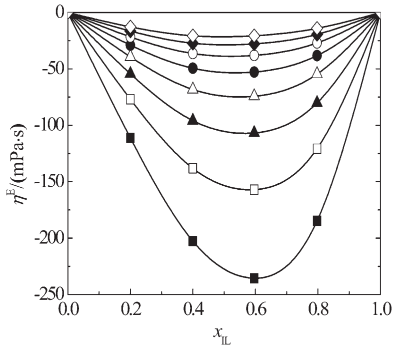

Figure 3. Relationship between x_{IL} and η^{E} for [BMIM][DMP] + methanol binary mixtures at different temperatures: ■, 298.15 K; □, 303.15 K; ▲, 308.15 K; △, 313.15 K; ●, 318.15 K; ○, 323.15 K; ♦, 328.15 K; ◊, 333.15 K.

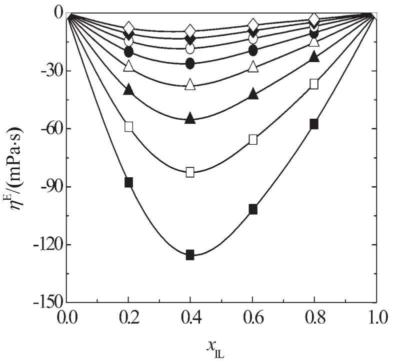

Figure 4. Relationship between x_{IL} and η^{E} for [BMIM][DMP] + water binary mixtures at different temperatures: ■, 298.15 K; □, 303.15 K; ▲, 308.15 K; △, 313.15 K; ●, 318.15 K; ○, 323.15 K; ♦, 328.15 K; ◊, 333.15 K.

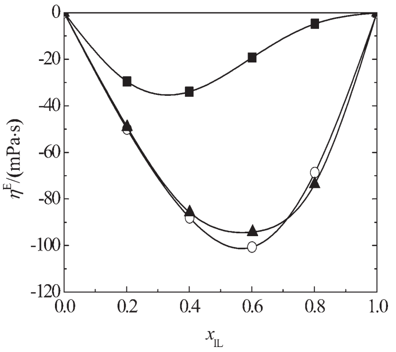

Figure 5. Excess viscosity, η^{E}, for three binary mixtures at 298.15 K: ■, [EMIM][DMP] + water; ○, [EMIM][DMP] + methanol; ▲, [EMIM][DMP] + ethanol.

viscosity η^{E} for the binary mixtures of IL plus methanol or ethanol are much higher than that of IL aqueous solution at any specific temperature, which cannot be explained by the small difference of viscosity of pure solvents ranging only from 0.53 to 1.04 at 298.15 K, and they all decrease with increasing temperature. In contrast, the difference of excess viscosity for (IL + methanol) and (IL + ethanol) mixtures is negligible for a specified IL, as manifested by Figure 5 for the IL [EMIM][DMP].

The results suggest that methanol or ethanol has a stronger ability to decrease the electrostatic interactions among ions or ionic clusters in the IL binary mixtures, leading to a much lower viscosity and larger deviation from the ideal solution behavior. This phenomenon can be explained by the larger separating ability of methanol or ethanol for the ionic species due to its larger molecule size, rather than the difference of dielectric behavior of different solvents.

Density of Pure Components. For the internal consistency and completeness of the experimental data, the densities of the pure components at atmospheric pressure in the temperature range of (293.15 to 333.15) K were also measured and are presented in Table 4. It is observed that the density of the pure components studied here follows the order of [EMIM][DMP] > [BMIM][DMP] > water > ethanol ≈ methanol at any temperature, and the volume expansivity calculated by $\alpha = 1/V(\partial V/\partial T)_{\text{P}} = -(\partial \ln \rho/\partial T)_{\text{P}}$ for pure components at 293.15 K follows the order of methanol ($1.24\cdot10^{-3}$ K^{-1}) > ethanol ($1.15\cdot10^{-3}$ K^{-1}) > [BMIM][DMP] ($5.70\cdot10^{-4}$ K^{-1}) > [EMIM][DMP] ($5.56\cdot10^{-4}$ K^{-1}) > water ($2.59\cdot10^{-4}$ K^{-1}). The higher density and lower expansivity of ILs may be attributed to the presence of electrostatic interaction among ionic species in an IL. In comparison with [BMIM][DMP], the IL [EMIM][DMP] has a little higher density, which is likely due to the stronger electrostatic interaction between the smaller cation $[\text{EMIM}]^+$ and the anion $[\text{DMP}]^-$, albeit the cation $[\text{BMIM}]^+$ has a higher dispersion energy due to its longer alkyl substitute.

Density Correlation for the Binary Mixtures. The density data for the IL-containing binary mixtures at the mole fraction of IL, x_{IL}, being about 0.2, 0.4, 0.6, and 0.8, were measured at the same pressure and temperature as that for the pure components

Table 4. Density Data Measured for the Pure Components at Atmospheric Pressure in the Temperature Range of (293.15 to 333.15) K

	density ρ ($g \cdot cm^{-3}$) at the following temperatures, T (K)								
component	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
ethanol	0.7901	0.7858	0.7815	0.7772	0.7728	0.7683	0.7639	0.7593	0.7547
methanol	0.7913	0.7866	0.7818	0.7771	0.7723	0.7675	0.7626	0.7577	0.7528
water	0.9982	0.9971	0.9957	0.9940	0.9922	0.9902	0.9881	0.9857	0.9831
[BMIM][DMP]	1.1653	1.1619	1.1586	1.1553	1.1520	1.1488	1.1455	1.1422	1.1390
[EMIM][DMP]	1.2234	1.2200	1.2166	1.2132	1.2098	1.2065	1.2031	1.1998	1.1965

Table 5. Density Data Measured for Six Binary Mixtures at Atmospheric Pressure and Different Temperatures and Mole Fractions of ILs

	density ρ ($g \cdot cm^{-3}$) at the following temperatures, T (K)								
x_{IL}	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15	333.15
				[EMIM][DMP] + Water					
0.201	1.1950	1.1914	1.1877	1.1840	1.1802	1.1765	1.1727	1.1688	1.1650
0.400	1.2179	1.2144	1.2110	1.2075	1.2041	1.2006	1.1971	1.1936	1.1901
0.601	1.2226	1.2192	1.2159	1.2125	1.2091	1.2057	1.2024	1.1990	1.1956
0.802	1.2233	1.2200	1.2166	1.2132	1.2099	1.2065	1.2032	1.1999	1.1965
				[BMIM][DMP] + Water					
0.201	1.1488	1.1452	1.1416	1.1379	1.1341	1.1303	1.1266	1.1228	1.1189
0.399	1.1629	1.1594	1.1560	1.1525	1.1490	1.1455	1.1420	1.1385	1.1351
0.602	1.1657	1.1624	1.1591	1.1557	1.1524	1.1490	1.1457	1.1423	1.1390
0.799	1.1657	1.1624	1.1591	1.1559	1.1525	1.1492	1.1459	1.1426	1.1393
				[EMIM][DMP] + Methanol					
0.201	1.0491	1.0453	1.0414	1.0376	1.0338	1.0299	1.0261	1.0223	1.0185
0.402	1.1349	1.1313	1.1276	1.1238	1.1202	1.1164	1.1126	1.1088	1.1050
0.601	1.1791	1.1756	1.1721	1.1686	1.1652	1.1617	1.1583	1.1549	1.1514
0.802	1.2071	1.2037	1.2002	1.1968	1.1934	1.1900	1.1866	1.1833	1.1800
				[BMIM][DMP] + Methanol					
0.200	1.0268	1.0229	1.0190	1.0155	1.0118	1.0080	1.0042	1.0005	0.9967
0.400	1.0982	1.0946	1.0911	1.0875	1.0839	1.0804	1.0768	1.0731	1.0693
0.596	1.1325	1.1291	1.1257	1.1223	1.1189	1.1155	1.1121	1.1087	1.1054
0.797	1.1523	1.1490	1.1456	1.1423	1.1390	1.1356	1.1323	1.1290	1.1257
				[EMIM][DMP] + Ethanol					
0.202	0.9988	0.9950	0.9912	0.9875	0.9837	0.9799	0.9761	0.9723	0.9686
0.402	1.0989	1.0953	1.0917	1.0881	1.0845	1.0810	1.0774	1.0738	1.0703
0.602	1.1582	1.1547	1.1512	1.1477	1.1442	1.1408	1.1373	1.1339	1.1305
0.801	1.1961	1.1927	1.1892	1.1858	1.1824	1.1790	1.1756	1.1723	1.1689
				[BMIM][DMP] + Ethanol					
0.200	0.9863	0.9826	0.9788	0.9751	0.9714	0.9677	0.9640	0.9602	0.9565
0.400	1.0690	1.0655	1.0619	1.0584	1.0549	1.0514	1.0479	1.0443	1.0408
0.601	1.1149	1.1115	1.1080	1.1046	1.1012	1.0978	1.0944	1.0910	1.0876
0.799	1.1447	1.1414	1.1381	1.1348	1.1314	1.1281	1.1248	1.1215	1.1182

and are presented in Table 5. The overall variation trend of the density with temperature and IL content for a binary mixture is presented in Figure 6, by taking the mixture of ([EMIM][DMP] + methanol) as an illustrative example. As shown in the figure, the densities of a mixture are always between that of the constituting pure components, that is, $\rho_{IL} > \rho_{mixture} > \rho_{solvent}$, decrease slightly in a linear way with the increasing temperature and increase rapidly with the IL content. In contrast to viscosity, density is much less sensitive to temperature.

In view of the linear variation with temperature and complex variation with IL content of the density for a binary mixture, the experimental data listed in Tables 4 and 5 are correlated with the following equations.[14]

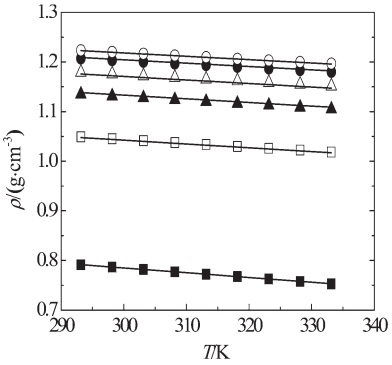

Figure 6. Experimental and correlative density of [EMIM][DMP] + methanol binary mixtures at different temperatures and mole fractions of IL: ■, 0; □, 0.201; ▲, 0.402; △, 0.601; ●, 0.802; ○, 1; —, calculated values from eq 5.

$$\rho = \alpha + \beta \cdot T \qquad (5)$$

$$\alpha = \sum_{i=1}^{5} a_i x_{IL}^{i-1} \qquad (6)$$

$$\beta = \sum_{i=1}^{5} b_i x_{IL}^{i-1} \qquad (7)$$

where ρ is the density in $g \cdot cm^{-3}$, T is the absolute temperature in K, a_i and b_i are the regression parameters, and x_{IL} is the mole fraction of IL. The regression parameters for each binary system were determined by the least-squares method and are listed in Table 6 along with the average absolute relative deviations (ARDs) of the correlation. It is showed that the experimental data of the density for all binary systems studied in the whole concentration range and in the temperature range of (293.15 to 333.15) K can be correlated satisfactorily.

Excess Molar Volume for the Binary Mixtures. The excess molar volume, V_m^E, is an important thermodynamic property to represent the nonideality of a solution, which is defined as the difference of the molar volume between the real mixture and an ideal solution at the same temperature, pressure, and composition, that is,

$$V_m^E = V_m - V_{m,id} \qquad (8)$$

where the molar volume of the binary mixture, V_m, and the molar volume for the same solution but at an ideal solution assumption,

Table 6. Parameters for the Correlation of Equations 5 to 7

correlation results	IL + solvent binary systems		
IL = [EMIM][DMP]	IL + water	IL + methanol	IL + ethanol
a_1	1.1107	1.0732	1.0500
a_2	2.7534	1.4644	1.1363
a_3	−8.0114	−2.8003	−1.7272
a_4	9.3644	2.5716	1.4540
a_5	−3.7976	−0.8883	−0.4928
b_1	$-3.7941 \cdot 10^{-4}$	$-9.6078 \cdot 10^{-4}$	$-8.8550 \cdot 10^{-4}$
b_2	$-3.6928 \cdot 10^{-3}$	$1.6532 \cdot 10^{-3}$	$9.8792 \cdot 10^{-4}$
b_3	$1.2141 \cdot 10^{-2}$	$-4.6144 \cdot 10^{-3}$	$-2.1330 \cdot 10^{-3}$
b_4	$-1.5011 \cdot 10^{-2}$	$5.7615 \cdot 10^{-3}$	$2.1812 \cdot 10^{-3}$
b_5	$6.2714 \cdot 10^{-3}$	$-2.5135 \cdot 10^{-3}$	$-8.2315 \cdot 10^{-4}$
ARD[a]	0.21 %	0.16 %	0.07 %
IL = [BMIM][DMP]	IL + water	IL + methanol	IL + ethanol
a_1	1.1112	1.0729	1.0497
a_2	2.3303	1.3159	1.0953
a_3	−6.8405	−2.7117	−1.9386
a_4	7.9832	2.6265	1.7974
a_5	−3.2271	−0.9458	−0.6463
b_1	$-3.8098 \cdot 10^{-4}$	$-9.5968 \cdot 10^{-4}$	$-8.8448 \cdot 10^{-4}$
b_2	$-3.5480 \cdot 10^{-3}$	$1.7039 \cdot 10^{-3}$	$1.0785 \cdot 10^{-3}$
b_3	$1.1374 \cdot 10^{-2}$	$-4.3955 \cdot 10^{-3}$	$-2.4194 \cdot 10^{-3}$
b_4	$-1.3749 \cdot 10^{-2}$	$5.1304 \cdot 10^{-3}$	$2.5624 \cdot 10^{-3}$
b_5	$5.6486 \cdot 10^{-3}$	$-2.1371 \cdot 10^{-3}$	$-9.9369 \cdot 10^{-4}$
ARD	0.19 %	0.18 %	0.08 %

[a] $\mathrm{ARD} = (1/n)\sum_{i=1}^{n} |\rho_{\mathrm{cal}}/\rho_{\mathrm{exp}} - 1.0|$.

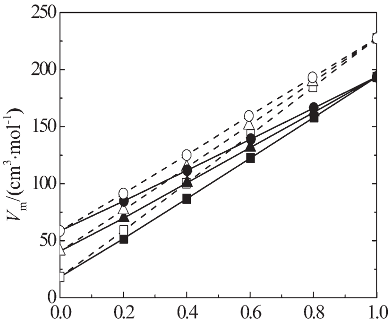

Figure 7. Molar volume versus mole fraction of IL for the binary mixtures at 298.15 K: ○, [BMIM][DMP] + ethanol; △, [BMIM][DMP] + methanol; □, [BMIM][DMP] + water; ●, [EMIM][DMP] + ethanol; ▲, [EMIM][DMP] + methanol; ■, [EMIM][DMP] + water.

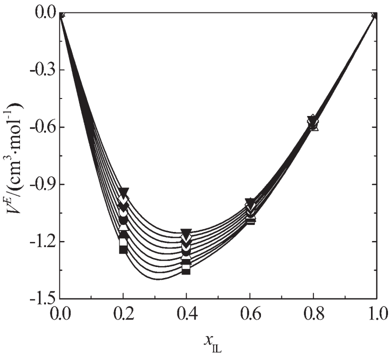

Figure 8. V^E versus x_{IL} for the Aqueous Solution of [BMIM][DMP] at different temperatures: ■, 293.15 K; □, 298.15 K; ▲, 303.15 K; △, 308.15 K; ●, 313.15 K; ○, 318.15 K; ◆, 323.15 K; ◇, 328.15 K; ▼, 333.15 K.

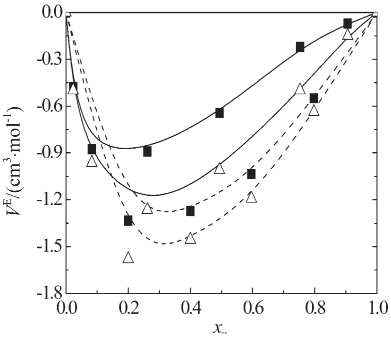

Figure 9. Compared results of V^E versus x_{IL} for the binary system IL + methanol at different temperatures: ■, 298.15 K; △, 323.15 K. Legend: — — —, [BMIM][DMP], this work; —, [BMIM][PF$_6$], taken from ref 15.

$V_{m,id}$, can be calculated as follows:

$$V_m = \frac{x_{IL} M_{IL} + x_S M_S}{\rho_{mix}} \tag{9}$$

$$V_{m,id} = \frac{x_{IL} M_{IL}}{\rho_{IL}} + \frac{x_S M_S}{\rho_S} \tag{10}$$

where M_S and M_{IL} are the mole masses of solvent and IL, respectively. x_S and x_{IL} represent the mole fractions of solvent and IL, respectively. ρ_s, ρ_{IL}, and ρ_{mix} refer to the densities of solvent, IL, and the mixed solution, respectively.

Figure 7 shows the molar volumes of the mixtures at 298.15 K against the mole fractions of IL for the six binary mixtures studied. It is obvious that the molar volumes of all mixtures increase linearly with the mole fractions of IL, with the linear correlation coefficient (R^2) being about 0.99. The results suggest that all of the binary mixtures studied here are close to the ideal solution behavior and thus their densities can be estimated accurately from the point of view of industrial application.

Based on the experimental data of density, as listed in Tables 4 and 5 and eqs 8 to 10, the excess molar volume for the binary mixtures studied was calculated at different conditions. As an example, a plot of excess molar volume against the mole fraction of IL at different temperatures for the aqueous solution of [BMIM][DMP] is presented in Figure 8. The results show that the excess volumes are negative for each system studied at any temperature and concentration, indicating a negative deviation from the ideal solution behavior. The excess volume is relatively low being in the range of (1.0 to 1.9) $\mathrm{cm^3 \cdot mol^{-1}}$ for all of the binary mixtures studied and reaches the maximum at the mole fraction of IL being around 0.3. Moreover, the excess volumes decrease as the temperature increasing for the (IL + water) mixtures, while the (IL+ alcohol) mixtures show an opposite trend. In addition, the effect of different ILs to the excess volume has been studied. As an example, a plot of excess volume against the mole fraction of IL for the methanol solution of [BMIM][DMP] and [BMIM][PF$_6$][15] is shown in Figure 9. The results show that the excess volume of [BMIM][DMP] + methanol binary system is much larger than that of [BMIM][PF$_6$] + methanol at atmospheric pressure with the same temperature and concentration. In effect, the excess volume is a reflection of the compromising effects among molecular sizes and various interactions for a specific mixture and is dependent on the temperature and composition. The negative excess volume may be attributed to the stronger ion−dipole interaction and charge transfer complexation between IL and the solvent molecules, as well as the interstitial effect in molecular packing due to the differences in the size and shape of the component molecules, by which the volume of the liquid mixture is apt to be contracted and reaches to the maximum at $x_{IL} \approx 0.3$ for all of the systems studied.

■ CONCLUSIONS

The viscosity and density data for six binary mixtures comprising of an IL, [EMIM][DMP] or [BMIM][DMP], and a solvent of water (methanol or ethanol) were measured at atmospheric pressure in the temperature range of (293.15 to 333.15) K using a viscometer and densimeter. The viscosity and density data were correlated by virtue of the Eyring equation and an empirical polynomial equation, respectively, with good accuracy. The excess viscosities and volumes are all negative in the whole temperature and concentration range studied, indicating a negative deviation from the ideality. In contrast to the monotonic decrease of the excess viscosity with increasing temperature, the variation of excess volume with temperature shows two opposite trends for the (IL + water) mixtures and the (IL + alcohol) mixtures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Comparative results for the viscosity and density of pure water for experimental and literature values at different temperatures; experimental information; and ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: licx@mail.buct.edu.cn. Tel./fax: +86 10 64410308.

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