Densities of Ionic Liquids, 1-Butyl-3-methylimidazolium Hexafluorophosphate and 1-Butyl-3-methylimidazolium Tetrafluoroborate, with Benzene, Acetonitrile, and 1-Propanol at T = (293.15 to 343.15) K

Yan Huo, Shuqian Xia, and Peisheng Ma*

Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

Densities of mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) with acetonitrile over the entire composition range at T = (293.15 to 343.15) K and with benzene and 1-propanol over the miscible composition range at T = (293.15 to 343.15) K were measured by a vibrating tube densimeter. Density measurements were used to compute the excess molar volumes, V^E. The V^E values have been fitted to the Redlich−Kister equation. V^E values are negative for all the mixtures over the miscible range and become more negative with increasing temperature. The V^E values for benzene mixtures are the most negative in the investigation.

Introduction

Room-temperature ionic liquids (RTILs) are a class of organic molten salts that are composed entirely of anions and cations.[1] Particularly, properties and data of the mixtures of ionic liquids with organic molecular solutes that are imperative for the design of many technological processes are very limited. The [BMIM][PF_6] and [BMIM][BF_4] are the most important investigated ionic liquids. In this paper, we report the densities for [BMIM][PF_6] and [BMIM][BF_4] with acetonitrile, benzene, and 1-propanol over several temperatures and at atmospheric pressure from which the excess molar volume V^E value has been calculated.

Experimental Section

Materials. [BMIM][PF_6] and [BMIM][BF_4] were obtained from Henan Lihua Pharmaceutical Co., Ltd with mass fraction of > 0.98, and they contained less than $2\cdot10^{-3}$ mass fraction water. These data were stated by the supplier. Ionic liquids were used after being vacuum desiccated for at least 4 h to remove trace amounts of water. Other chemicals used in this study were supplied by Tianjin Reagent Co., although the organic solvents were dried over 0.4 nm molecular sieves and degassed by ultrasound prior to their use. The mass fraction purities determined by gas chromatography were as follows: acetonitrile (> 0.998), benzene (> 0.998), 1-propanol (> 0.998). During the course of the experiments, the purity of the solvents was monitored by density measurements.

Apparatus and Procedure. The densities of the pure components and their mixtures were measured with a high precision vibrating tube digital density meter (density/specific gravity meter DA 505, KEM, Japan) whose measurement cell temperature was controlled automatically within ± 0.01 K of the selected value. The uncertainty in density measurements was ± $5\cdot10^{-5}$ g·cm^{-3}. Density measurements were reproducible to ± $3\cdot10^{-5}$ g·cm^{-3}.

* To whom correspondence should be addressed. E-mail: mapeisheng@tju.edu.cn.

The liquid mixtures were prepared by mass using a BP210s balance accurate to within ± 0.01 mg. The average uncertainty in the mole fraction of the mixtures was estimated to be less than ± 0.0001. The molar excess volumes were calculated from composition density data with an uncertainty greater than ± 0.002 cm^3·mol^{-1}. All molar quantities were based on the IUPAC relative atomic mass table.

Results and Discussion

In the experiments, the densities for one composition were measured at different temperatures. Densities of pure compounds were reported in Table 1 together with the corresponding literature values. For the densities, good agreement was found between the measured and literature values for all these pure substances. There was an appreciable difference for the density data among the various literature for [BMIM][BF_4] because of the different water content.

The experimental density ρ data for the acetonitrile (1) + [BMIM][PF_6] (2), acetonitrile (1) + [BMIM][BF_4] (2), benzene (1) + [BMIM][PF_6] (2), benzene (1) + [BMIM][BF_4] (2), 1-propanol (1) + [BMIM][BF_4] (2) mixtures, as a function of [BMIM][PF_6] or [BMIM][BF_4] mole fraction (x_2) at the temperature range T = (293.15 to 343.15) K are presented respectively in Table 2.

Values of excess molar volume (V^E) were calculated using the following relation:[2]

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (1)$$

where x_i, M_i, and ρ_i are mole fractions, molar mass, and densities of component i, respectively, and ρ is the density of mixture. Subscript i = 1 is for the organic solvents (acetonitrile, benzene, or 1-propanol), and i = 2 is for the ionic liquids ([BMIM][PF_6] or [BMIM][BF_4]).

10.1021/je700266n CCC: $37.00
Published on Web 07/28/2007

Table 1. Comparison of Experimental and Literature Values of Densities ρ for Pure Compouds

		ρ/g·cm^{-3}				ρ/g·cm^{-3}	
liquid	T/K	exptl	ref	ionic liquid	T/K	exptl	ref[a]
benzene	298.15	0.87311	0.87357[3]	[BMIM][BF_4]	293.15	1.19571	1.2046[8]
	303.15	0.86759	0.86821[3]		298.15	1.19207	1.20503[6]
	313.15	0.85682	0.85734[3]				1.19[7]
	323.15	0.84605	0.84665[2]				1.2015[8]
					303.15	1.18837	1.20129[6]
acetonitrile	298.15	0.77693	0.77653[2]				1.1984[8]
	303.15	0.77144	0.77112[2]		308.15	1.18472	1.1954[8]
	308.15	0.76597	0.76566[2]		313.15	1.18143	1.19459[8]
	313.15	0.76068	0.76016[2]				1.1922[8]
					323.15	1.17449	1.18785[6]
1-propanol	293.15	0.80497	0.80364[5]				1.1860[8]
	303.15	0.79689	0.79548[5]		333.15	1.16689	1.1798[8]
			0.7956[9]		343.15	1.15997	1.1735[8]
	313.15	0.78907	0.78702[5]	[BMIM][PF_6]	298.15	1.36722	1.36666[2]
			0.7876[9]				1.3660[6]
	323.15	0.78074	0.7791[9]		303.15	1.36286	1.36240[2]
	333.15	0.77175	0.7706[9]				1.3618[6]
					308.15	1.35856	1.3577[6]
					313.15	1.35430	1.35419[2]
							1.3535[6]
					323.15	1.34598	1.3453[6]

[a] Ref 6 reported that the water content of ILs was less than $75 \cdot 10^{-6}$; ref 8 reported that the water content of ILs was $200 \cdot 10^{-6}$. Other references did not report water content.

Table 2. Densities, ρ, and Excess Molar Volumes, V^E, for the Binary Mixtures at Different Temperatures

x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}
	(x_2)[BMIM][BF_4] + $(1-x_2)$acetonitrile						(x_2)[BMIM][PF_6] + $(1-x_2)$acetonitrile				
	T = 293.15 K						T = 293.15 K				
0.0000	0.78230	0.0000	0.6015	1.13887	−0.8730	0.0000	0.78230	0.0000	0.5996	1.29348	−0.8020
0.1000	0.91354	−0.9460	0.6998	1.15673	−0.6406	0.1000	0.97406	−0.8408	0.7001	1.31851	−0.5637
0.1997	0.99350	−1.2439	0.7990	1.17164	−0.4010	0.1997	1.08947	−1.1234	0.8000	1.33925	−0.3641
0.3000	1.04776	−1.2984	0.9012	1.18523	−0.2554	0.3001	1.16716	−1.2178	0.8992	1.35681	−0.2139
0.4005	1.08695	−1.2417	1.0000	1.19571	0.0000	0.4002	1.22132	−1.1104	1.0000	1.37157	0.0000
0.4995	1.11642	−1.1530				0.4995	1.26157	−0.9524			
	T = 298.15 K						T = 298.15 K				
0.0000	0.77693	0.0000	0.6015	1.13503	−0.9123	0.0000	0.77693	0.0000	0.5996	1.28908	−0.8495
0.1000	0.90878	−0.9887	0.6998	1.15298	−0.6740	0.1000	0.96905	−0.8862	0.7001	1.31415	−0.6024
0.1997	0.98903	−1.2947	0.7990	1.16796	−0.4272	0.1997	1.08437	−1.1585	0.8000	1.33492	−0.3935
0.3000	1.04355	−1.3537	0.9012	1.18158	−0.2700	0.3001	1.16248	−1.2762	0.8992	1.35254	−0.2390
0.4005	1.08289	−1.2932	1.0000	1.19207	0.0000	0.4002	1.21677	−1.1681	1.0000	1.36722	0.0000
0.4995	1.11251	−1.2027				0.4995	1.25710	−1.0052			
	T = 303.15 K						T = 303.15 K				
0.0000	0.77144	0.0000	0.6015	1.13108	−0.9486	0.0000	0.77144	0.0000	0.5996	1.28455	−0.8876
0.1000	0.90394	−1.0353	0.6998	1.14911	−0.7020	0.1000	0.9639	−0.9307	0.7001	1.30969	−0.6332
0.1997	0.98451	−1.3514	0.7990	1.16416	−0.4467	0.1997	1.07944	−1.2148	0.8000	1.33047	−0.4104
0.3000	1.03925	−1.4112	0.9012	1.17780	−0.2748	0.3001	1.15773	−1.3365	0.8992	1.34819	−0.2554
0.4005	1.07874	−1.3460	1.0000	1.18837	0.0000	0.4002	1.21210	−1.2217	1.0000	1.36286	0.0000
0.4995	1.10844	−1.2454				0.4995	1.25255	−1.0559			
	T = 308.15 K						T = 308.15 K				
0.0000	0.76597	0.0000	0.6015	1.12717	−0.9854	0.0000	0.76597	0.0000	0.5996	1.28012	−0.9322
0.1000	0.89910	−1.0813	0.6998	1.14529	−0.7313	0.1000	0.95879	−0.9773	0.7001	1.30551	−0.6928
0.1997	0.98003	−1.4104	0.7990	1.16039	−0.4642	0.1997	1.07457	−1.2745	0.8000	1.32623	−0.4484
0.3000	1.03499	−1.4707	0.9012	1.17409	−0.2831	0.3001	1.15301	−1.3973	0.8992	1.34383	−0.2622
0.4005	1.07462	−1.3994	1.0000	1.18472	0.0000	0.4002	1.20752	−1.2807	1.0000	1.35856	0.0000
0.4995	1.10446	−1.2944				0.4995	1.24807	−1.1101			
	T = 313.15 K						T = 313.15 K				
0.0000	0.76068	0.0000	0.6015	1.12364	−1.0290	0.0000	0.76068	0.0000	0.5996	1.27612	−1.0184
0.1000	0.89451	−1.1300	0.6998	1.14182	−0.7625	0.1000	0.95396	−1.0334	0.7001	1.30133	−0.7454
0.1997	0.97582	−1.4715	0.7990	1.15700	−0.4868	0.1997	1.07004	−1.3511	0.8000	1.32221	−0.5093
0.3000	1.03110	−1.5390	0.9012	1.17073	−0.2909	0.3001	1.14867	−1.4820	0.8992	1.33974	−0.3016
0.4005	1.07084	−1.4574	1.0000	1.18143	0.0000	0.4002	1.20329	−1.3648	1.0000	1.35430	0.0000
0.4995	1.10065	−1.3281				0.4995	1.24397	−1.1962			
	T = 323.15 K						T = 323.15 K				
0.0000	0.74973	0.0000	0.6015	1.11623	−1.1232	0.0000	0.74973	0.0000	0.5996	1.26765	−1.1335
0.1000	0.88505	−1.2386	0.6998	1.13455	−0.8334	0.1000	0.94395	−1.1458	0.7001	1.29268	−0.8036
0.1997	0.96707	−1.6049	0.7990	1.14988	−0.5378	0.1997	1.06053	−1.4899	0.8000	1.31373	−0.5546
0.3000	1.02286	−1.6756	0.9012	1.16380	−0.3308	0.3001	1.13957	−1.6302	0.8992	1.33133	−0.3230

Table 2. (Continued)

x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}
0.4005	1.06298	−1.5876	1.0000	1.17449	0.0000	0.4002	1.19450	−1.5105	1.0000	1.34598	0.0000
0.4995	1.09319	−1.4598				0.4995	1.23537	−1.3292			
		T = 333.15 K					T = 333.15 K				
0.0000	0.73819	0.0000	0.6015	1.10814	−1.2221	0.0000	0.73819	0.0000	0.5996	1.25864	−1.2047
0.1000	0.87491	−1.2386	0.6998	1.12663	−0.9111	0.1000	0.93335	−1.2604	0.7001	1.28391	−0.8589
0.1997	0.95771	−1.7520	0.7990	1.14209	−0.5911	0.1997	1.05042	−1.6227	0.8000	1.30514	−0.5912
0.3000	1.01398	−1.8242	0.9012	1.15607	−0.3513	0.3001	1.12980	−1.7562	0.8992	1.32302	−0.3593
0.4005	1.05445	−1.7266	1.0000	1.16689	0.0000	0.4002	1.18499	−1.6173	1.0000	1.33770	0.0000
0.4995	1.08493	−1.5749				0.4995	1.22609	−1.4148			
		T = 343.15 K					T = 343.15 K				
0.0000	0.72694	0.0000	0.6015	1.10067	−1.3273	0.0000	0.72694	0.0000	0.5996	1.25062	−1.2617
0.1000	0.86642	−1.5800	0.6998	1.11931	−0.9884	0.1000	0.92324	−1.3789	0.7001	1.27641	−0.9258
0.1997	0.94885	−1.9111	0.7990	1.13492	−0.6427	0.1997	1.04099	−1.7598	0.8000	1.29784	−0.6345
0.3000	1.00539	−1.9598	0.9012	1.14906	−0.3814	0.3001	1.12072	−1.8734	0.8992	1.31594	−0.3863
0.4005	1.04632	−1.8569	1.0000	1.15997	0.0000	0.4002	1.17643	−1.7273	1.0000	1.33076	0.0000
0.4995	1.07727	−1.7182				0.4995	1.21782	−1.4989			
		(x_2)[BMIM][BF$_4$] + (1−x_2)benzene					(x_2)[BMIM][PF6] + (1−x_2)benzene				
		T = 293.15 K					T = 293.15 K				
0.0000	0.87823	0.0000	0.8000	1.16873	−0.9308	0.0000	0.87823	0.0000	0.7000	1.30429	−1.2330
0.4871	1.10520	−1.8411	0.8990	1.18280	−0.4588	0.3400	1.16634	−2.1019	0.8003	1.32979	−0.8227
0.5499	1.12099	−1.7394	0.9498	1.18944	−0.2228	0.3995	1.19759	−2.2168	0.9001	1.35151	−0.3427
0.5999	1.13231	−1.6357	1.0000	1.19571	0.0000	0.4999	1.23920	−1.8918	1.0000	1.37157	0.0000
0.7001	1.15184	−1.2957				0.5999	1.27425	−1.5676			
		T = 298.15 K					T = 298.15 K				
0.0000	0.87311	0.0000	0.8000	1.16502	−0.9616	0.0000	0.87311	0.0000	0.7000	1.29995	−1.2817
0.4871	1.10128	−1.9063	0.8990	1.17915	−0.4780	0.3400	1.16180	−2.1780	0.8003	1.32597	−0.8600
0.5499	1.11714	−1.7888	0.9498	1.18585	−0.2408	0.3995	1.19315	−2.2668	0.9001	1.34729	−0.3696
0.5999	1.12850	−1.6931	1.0000	1.19207	0.0000	0.4999	1.23486	−1.9633	1.0000	1.36722	0.0000
0.7001	1.14813	−1.3569				0.5999	1.26999	−1.6338			
		T = 303.15 K					T = 303.15 K				
0.0000	0.86759	0.0000	0.8000	1.16124	−0.9988	0.0000	0.86759	0.0000	0.7000	1.29560	−1.3436
0.4871	1.09721	−1.9802	0.8990	1.17538	−0.4920	0.3400	1.15716	−2.2683	0.8003	1.32158	−0.8963
0.5499	1.11320	−1.8642	0.9498	1.18212	−0.2485	0.3995	1.18862	−2.3615	0.9001	1.34285	−0.3780
0.5999	1.12457	−1.7584	1.0000	1.18837	0.0000	0.4999	1.23038	−2.0462	1.0000	1.36286	0.0000
0.7001	1.14426	−1.4059				0.5999	1.26561	−1.7107			
		T = 308.15 K					T = 308.15 K				
0.0000	0.86221	0.0000	0.8000	1.15748	−1.0304	0.0000	0.86221	0.0000	0.7000	1.29134	−1.4079
0.4871	1.09323	−2.0558	0.8990	1.17167	−0.5069	0.3400	1.15256	−2.3524	0.8003	1.31728	−0.9356
0.5499	1.10930	−1.9356	0.9498	1.17845	−0.2574	0.3995	1.18416	−2.4538	0.9001	1.33855	−0.3975
0.5999	1.12071	−1.8236	1.0000	1.18472	0.0000	0.4999	1.22601	−2.1323	1.0000	1.35856	0.0000
0.7001	1.14047	−1.4571				0.5999	1.26130	−1.7866			
		T = 313.15 K					T = 313.15 K				
0.0000	0.85682	0.0000	0.8000	1.15413	−1.0768	0.0000	0.85682	0.0000	0.7000	1.28735	−1.5058
0.4871	1.08958	−2.1469	0.8990	1.16835	−0.5301	0.3400	1.14835	−2.4810	0.8003	1.31309	−0.9866
0.5499	1.10572	−2.0186	0.9498	1.17516	−0.2713	0.3995	1.18004	−2.5856	0.9001	1.33445	−0.4415
0.5999	1.11722	−1.9053	1.0000	1.18143	0.0000	0.4999	1.22202	−2.2638	1.0000	1.35430	0.0000
0.7001	1.13704	−1.5196				0.5999	1.25739	−1.9120			
		T = 323.15 K					T = 323.15 K				
0.0000	0.84605	0.0000	0.8000	1.14703	−1.1597	0.0000	0.84605	0.0000	0.7000	1.27903	−1.6383
0.4871	1.08190	−2.3149	0.8990	1.16136	−0.5762	0.3400	1.13950	−2.6858	0.8003	1.30476	−1.0732
0.5499	1.09823	−2.1787	0.9498	1.16819	−0.2934	0.3995	1.17145	−2.8031	0.9001	1.32620	−0.4960
0.5999	1.10981	−2.0507	1.0000	1.17449	0.0000	0.4999	1.21365	−2.4703	1.0000	1.34598	0.0000
0.7001	1.12983	−1.6399				0.5999	1.24914	−2.0946			
		T = 333.15 K					T = 333.15 K				
0.0000	0.83576	0.0000	0.8000	1.13928	−1.2248	0.0000	0.83576	0.0000	0.7000	1.27076	−1.7626
0.4871	1.07373	−2.4527	0.8990	1.15364	−0.6016	0.3400	1.12994	−2.7802	0.8003	1.29668	−1.1839
0.5499	1.09017	−2.3058	0.9498	1.16054	−0.3075	0.3995	1.16213	−2.9088	0.9001	1.31785	−0.5263
0.5999	1.10175	−2.1576	1.0000	1.16689	0.0000	0.4999	1.20495	−2.6144	1.0000	1.33770	0.0000
0.7001	1.12195	−1.7292				0.5999	1.24067	−2.2308			
		T = 343.15 K					T = 343.15 K				
0.0000	0.82489	0.0000	0.8000	1.13217	−1.3127	0.0000	0.82489	0.0000	0.7000	1.26366	−1.9244
0.4871	1.06572	−2.5966	0.8990	1.14664	−0.6478	0.3400	1.12087	−2.9086	0.8003	1.28979	−1.3135
0.5499	1.08251	−2.4602	0.9498	1.15358	−0.3304	0.3995	1.15345	−3.0513	0.9001	1.31077	−0.5659
0.5999	1.09435	−2.3196	1.0000	1.15997	0.0000	0.4999	1.19696	−2.7805	1.0000	1.33076	0.0000
0.7001	1.11470	−1.8548				0.5999	1.23313	−2.3938			
		(x_2)[BMIM][BF$_4$] + (1−x_2)1-propanol					(x_2)[BMIM][BF$_4$] + (1−x_2)1-propanol				
		T = 293.15 K					T = 313.15 K				
0.0000	0.80497	0.0000	0.6978	1.14141	−0.3752	0.0000	0.78907	0.0000	0.6978	1.12678	−0.4235
0.3999	1.05466	−0.4988	0.8002	1.16300	−0.3388	0.3999	1.03988	−0.6112	0.8002	1.14861	−0.3900

Table 2. (Continued)

x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}	x	ρ / g·cm^{-3}	V^E / cm^3·mol^{-1}
0.4498	1.07268	−0.4986	0.9003	1.18065	−0.1978	0.4498	1.05772	−0.5775	0.9003	1.16626	−0.2156
0.5001	1.08908	−0.4819	1.0000	1.19571	0.0000	0.5001	1.07409	−0.5475	1.0000	1.18143	0.0000
0.6001	1.11770	−0.4372				0.6001	1.10301	−0.5037			
		T = 298.15 K						T = 323.15 K			
0.0000	0.80101	0.0000	0.6978	1.13771	−0.3884	0.0000	0.78074	0.0000	0.6978	1.11964	−0.4625
0.3999	1.05103	−0.5370	0.8002	1.15935	−0.3523	0.3999	1.03241	−0.6711	0.8002	1.14154	−0.4170
0.4498	1.06890	−0.5171	0.9003	1.17699	−0.2026	0.4498	1.05032	−0.6356	0.9003	1.15925	−0.2282
0.5001	1.08528	−0.4991	1.0000	1.19207	0.0000	0.5001	1.06673	−0.6001	1.0000	1.17449	0.0000
0.6001	1.11399	−0.4518				0.6001	1.09573	−0.5452			
		T = 303.15 K						T = 333.15 K			
0.0000	0.79689	0.0000	0.6978	1.13391	−0.3995	0.0000	0.77175	0.0000	0.6978	1.11183	−0.5046
0.3999	1.04717	−0.5624	0.8002	1.15561	−0.3638	0.3999	1.02428	−0.7382	0.8002	1.13381	−0.4473
0.4498	1.06503	−0.5380	0.9003	1.17325	−0.2054	0.4498	1.04229	−0.7044	0.9003	1.15158	−0.2425
0.5001	1.08139	−0.5142	1.0000	1.18837	0.0000	0.5001	1.05877	−0.6669	1.0000	1.16689	0.0000
0.6001	1.11015	−0.4654				0.6001	1.08782	−0.5963			
		T = 308.15 K						T = 343.15 K			
0.0000	0.79283	0.0000	0.6978	1.13015	−0.4090	0.0000	0.76286	0.0000	0.6978	1.10468	−0.5613
0.3999	1.04337	−0.5887	0.8002	1.15192	−0.3752	0.3999	1.01675	−0.8307	0.8002	1.12678	−0.4920
0.4498	1.06122	−0.5599	0.9003	1.16956	−0.2081	0.4498	1.03483	−0.7916	0.9003	1.14459	−0.2624
0.5001	1.07757	−0.5314	1.0000	1.18472	0.0000	0.5001	1.05138	−0.7487	1.0000	1.15997	0.0000
0.6001	1.10639	−0.4827				0.6001	1.08057	−0.6678			

Table 3. Coefficients of the Redlich−Kister Equation and Standard Deviation for Excess Molar Volumes of Mixtures

T/K	A_0	A_1	A_2	A_3	AAD	SD
			(x_2)[BMIM][BF$_4$] + (1−x_2)acetonitrile			
293.15	−4.3270	3.7127	−2.7914	1.7312	0.053	0.038
298.15	−4.5131	3.8178	−2.9660	1.8468	0.051	0.040
303.15	−4.6889	3.9559	−3.1401	2.0565	0.049	0.039
308.15	−4.8748	4.1135	−3.3022	2.2179	0.048	0.040
313.15	−5.0579	4.2808	−3.5374	2.3766	0.044	0.037
323.15	−5.2503	4.6477	−3.9407	2.5464	0.047	0.045
333.15	−6.0028	4.9943	−4.3543	3.0211	0.044	0.047
343.15	−6.4341	5.0119	−5.3493	4.8990	0.057	0.067
			(x_2)[BMIM][PF$_6$] + (1−x_2)acetonitrile			
293.15	−3.8221	3.5087	−2.7334	1.3517	0.032	0.019
298.15	−4.0282	3.5882	−2.8764	1.3760	0.035	0.025
303.15	−4.2167	3.7595	−3.0488	1.4322	0.036	0.026
308.15	−4.4413	3.7479	−3.2435	1.8345	0.028	0.023
313.15	−5.7703	3.8613	−3.4994	1.8302	0.029	0.026
323.15	−5.2805	3.2738	−3.7223	2.1478	0.033	0.032
333.15	−5.6154	4.6553	−4.3791	2.4280	0.035	0.036
343.15	−5.9392	4.9721	−5.0893	2.8944	0.033	0.036
			(x_2)[BMIM][BF$_4$] + (1−x_2)benzene			
293.15	−7.3037	2.8355	−1.0126	1.1904	0.008	0.009
298.15	−7.5436	2.9297	−1.4085	1.5135	0.007	0.007
303.15	−7.8451	3.0056	−1.2282	1.4135	0.008	0.008
308.15	−8.1446	3.0881	−0.9800	1.2242	0.008	0.007
313.15	−8.5035	3.2347	−0.9814	1.1695	0.009	0.009
323.15	−9.1703	3.5050	−1.0061	1.1154	0.007	0.007
333.15	−9.7119	4.0790	−2.0783	2.0025	0.008	0.008
343.15	−10.304	3.4110	0.0042	0.6231	0.008	0.009
			(x_2)[BMIM][PF$_6$] + (1−x_2)benzene			
293.15	−7.7007	5.3887	−1.5841	0.4256	0.033	0.045
298.15	−7.9586	5.4432	−1.7611	0.5801	0.026	0.038
303.15	−8.3010	5.5604	−1.9247	1.0716	0.026	0.040
308.15	−8.6511	5.6802	−1.8634	1.0731	0.026	0.041
313.15	−9.1941	5.8683	−1.5466	0.6754	0.020	0.038
323.15	−10.036	6.3190	−1.0506	−0.1235	0.016	0.038
333.15	−10.568	5.9327	−0.9590	0.5309	0.019	0.037
343.15	−11.206	5.5239	−1.3347	1.8354	0.021	0.041
			(x_2)[BMIM][BF$_4$] + (1−x_2)1-propanol			
293.15	−1.9148	0.7014	−1.1299	−0.4701	0.021	0.009
298.15	−1.9773	0.9130	−2.0695	0.4047	0.020	0.009
303.15	−2.0407	1.0318	−2.5042	0.8070	0.021	0.010
308.15	−2.1141	1.1406	−2.7997	1.0706	0.023	0.012
313.15	−2.1846	1.1732	−3.0454	1.3053	0.023	0.012
323.15	−2.3918	1.3371	−3.3699	1.5729	0.022	0.012
333.15	−2.6505	1.4913	−3.3032	1.4106	0.021	0.013
343.15	−2.9767	1.7070	−3.6654	1.7029	0.021	0.014

The V^E values have been fitted to the Redlich−Kister equation[4]

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = x_2(1-x_2)\sum_k A_k(1-2x_2)^k \qquad (2)$$

In each case, the optimum number of coefficients A_k was determined from an examination of the variation of the average absolute derivations (AAD) and standard derivations (SD):

$$\text{AAD} = \frac{\sum |(V^E_{\text{cal}} - V^E_{\text{exp}})/V^E_{\text{exp}}|}{n} \qquad (3)$$

$$\text{SD} = [\sum (V^E_{cal} - V^E_{\text{exp}})^2/(n-1)]^{(1/2)} \qquad (4)$$

where n is the total number of experimental values.

It is found that the Redlich−Kister (RK) equation represents satisfactorily the experimental excess molar volumes for the studied systems. The polynomial coefficients A_k of eq 2 for the studied systems along with the average absolute derivations and standard derivations are collected in Table 3.

The excess molar volume data is presented in Table 2, and they are shown graphically in Figures 1, 2, and 3. It can be seen from Figure 1 that the V^E values for these two binary mixtures over the whole composition range are negative. The absolute values of V^E increase with increasing temperature. The RK equation fitting curves are asymmetric. It is obvious that a minimum in V^E is reached with mole fraction of these ionic liquids near to 0.3 for acetonitrile (1) + [BMIM][PF$_6$] (2) and acetonitrile (1) + [BMIM][BF$_4$] (2) systems, respectively. In the experiment, it is found that immiscible mixtures appear with a mole fraction of benzene near to 0.3 for benzene (1) + [BMIM][PF$_6$] (2) and near to 0.5 for benzene (1) + [BMIM][BF$_4$] (2) systems. It is also obvious that a mole fraction of 1-propanol reaches 0.4 for 1-propanol (1) + [BMIM][BF$_4$] (2) systems when immiscible mixture appear. Because benzene and 1-propanol

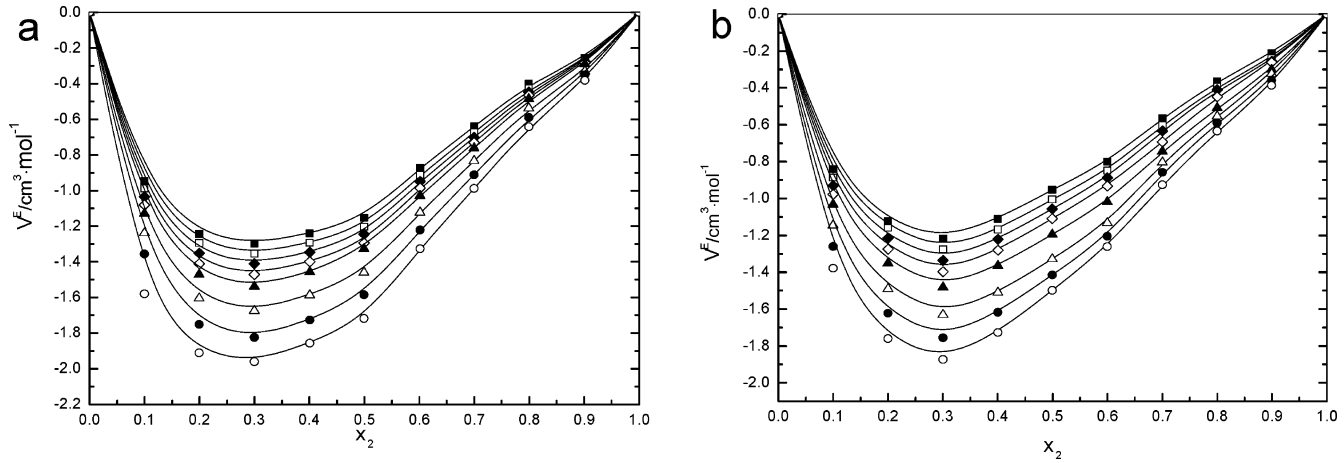

Figure 1. Excess molar volume variation with mole fraction to systems (a) acetonitrile (1) + [BMIM][BF_4] (2) and (b) acetonitrile (1) + [BMIM][PF_6] (2) for the following experimental values: ■, 293.15 K; □, 298.15 K; ◆, 303.15 K; ◇, 308.15 K; ▲, 313.15 K; △, 323.15 K; ●, 333.15 K; ○, 343.15 K; solid line, Redlich−Kister (eq 2).

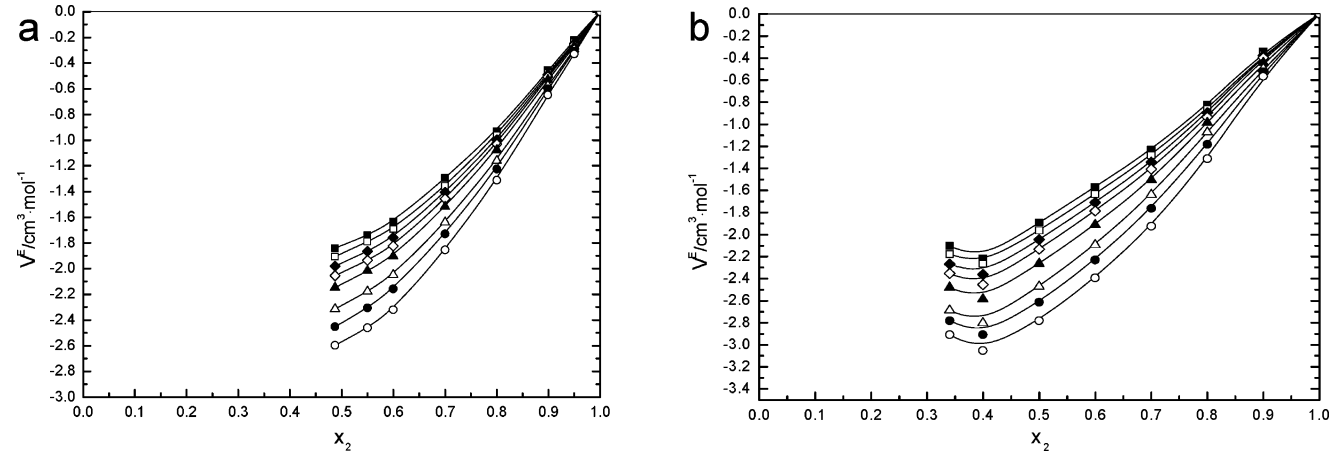

Figure 2. Excess molar volume variation with mole fraction to systems (a) benzene (1) + [BMIM][BF_4] (2) and (b) benzene (1) + [BMIM][PF_6] (2) for the following experimental values: ■, 293.15 K; □, 298.15 K; ◆, 303.15 K; ◇, 308.15 K; ▲, 313.15 K; △, 323.15 K; ●, 333.15 K; ○, 343.15 K; solid line, Redlich−Kister (eq 2).

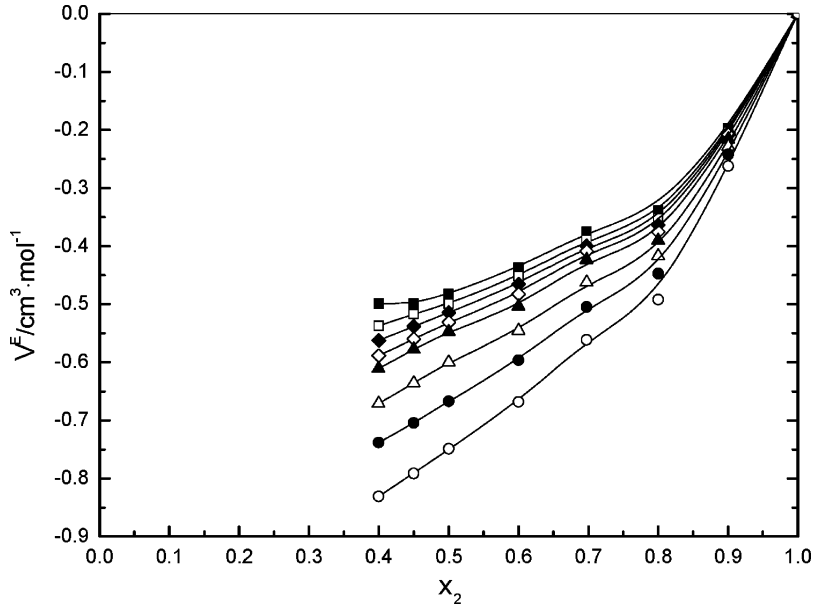

Figure 3. Excess molar volume variation with mole fraction to systems 1-propanol (1) + [BMIM][BF_4] (2) for the following experimental values: ■, 293.15 K; □, 298.15 K; ◆, 303.15 K; ◇, 308.15 K; ▲, 313.15 K; △, 323.15 K; ●, 333.15 K; ○, 343.15 K; solid line, Redlich−Kister (eq 2).

is only partically miscible in [BMIM][PF_6] and [BMIM][BF_4], the experimental V^E values are shown in their miscible range. As can be seen from Figure 4, the V^E values for benzene mixtures are more negative than any other mixtures at 298.15 K. The V^E values for [BMIM][PF_6] mixtures are as negative as the [BMIM][BF_4] mixtures at 298.15 K.

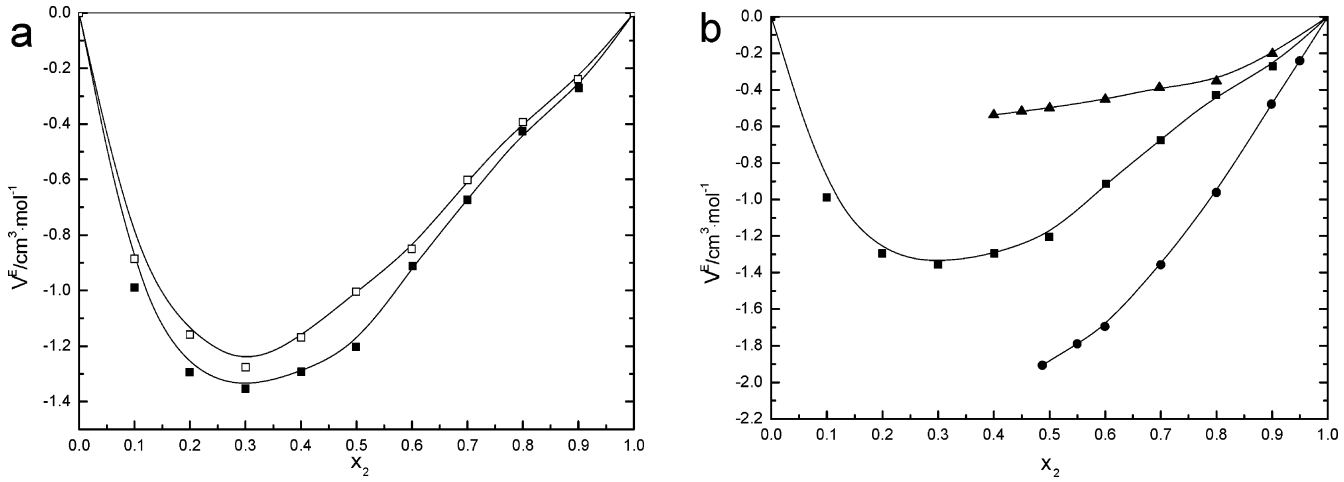

Figure 4. Excess molar volume variation with mole fraction to systems (a) ■, acetonitrile (1) + [BMIM][BF_4] (2); □, acetonitrile (1) + [BMIM][PF_6] (2); and (b) ■, acetonitrile (1) + [BMIM][BF_4] (2); ●, benzene (1) + [BMIM][BF_4] (2); ▲, 1-propanol (1) + [BMIM][BF_4] (2) for experimental values at 298.15 K; solid line, Redlich−Kister (eq 2).

Conclusions

Densities of the binary systems of ionic liquids ([BMIM][PF_6] or [BMIM][BF_4]) and organic solvents (acetonitrile, benzene, or 1-propanol) have been measured at several temperatures and for the miscible range. The excess molar volumes were computed at T = (293.15 to 343.15) K. The computed quantities have been fitted to the Redlich−Kister equation. V^E values are negatives for all the mixtures over the miscible range and become more negative with increasing temperature. The V^E values for benzene mixtures are the most negative in the investigation.

Literature Cited

(1) Marsh, K. N.; Boxall, J. A.; Lichtenthaler, R. Room temperature ionic liquids and their mixtures-a review. *Fluid Phase Equilib.* **2004**, *219*, 93−98.

(2) Zafarani-Moattar, M. T.; Shekaari, H. Volumetric and speed of sound of ionic liquid, 1-butyl-3-methyl-imidazolium hexafluorophosphate with acetonitrile and methanol at T = (298.15 to 318.15) K. *J. Chem. Eng. Data* **2005**, *50*, 1694−1699.

(3) Yang, C.; Ma, P.; Zhou, Q. Excess molar volumes and viscosities of binary mixtures of sulfolane with benzene, toluene, ethylbenzene, *p*-xylene, *o*-xylene, and *m*-xylene at (303.15 and 323.15) K and atmospheric pressure. *J. Chem. Eng. Data* **2004**, *49*, 881−885.

(4) Yang, C.; Lai, H.; Liu, Z.; Ma, P. Densities and viscosities of diethyl carbonate + toluene, + methanol, and +2-propanol from (293.15 to 363.15) K. *J. Chem. Eng. Data* **2006**, *51*, 584−589.

(5) Djojoputro, H.; Ismadji, S. Density and viscosity of binary mixtures of ethyl-2-methylbutyrate and ethyl hexanoate with methanol, ethanol, and 1-propanol at (293.15, 303.15, and 313.15) K. *J. Chem. Eng. Data* **2005**, *50*, 1343−1347.

(6) Gomes de Azevedo, R.; Esperanca, J. M. S. S.; Najdanovic-Visak, V. Thermophysical and thermodynamic properties of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate over an extended pressure range. *J. Chem. Eng. Data* **2005**, *50*, 997−1008.

(7) Zhang, S.; Sun, N.; He, X.; Lu, X.; Zhang, X. Physical properties of ionic liquids: database and evaluation. *J. Phys. Chem. Ref. Data* **2006**, *35*, 1475−1517.

(8) Zhou, Q.; Wang, L.-S.; Chen, H.-P. Densities and Viscosities of 1-Butyl-3-methylimidazolium Tetrafluoroborate + H_2O Binary Mixtures from (303.15 to 353.15) K. *J. Chem. Eng. Data* **2006**, *51*, 905−908.

(9) Zeberg-Mikkelsen, C. K.; Andersen, S. I. Density Measurements under Pressure for the Binary System 1-Propanol + Toluene. *J. Chem. Eng. Data* **2005**, *50*, 524−528.

Received for review May 14, 2007. Accepted June 26, 2007. We are very grateful to project 863, China, for the assistance of fund 2006AA06Z376.

JE700266N