JOURNAL OF CHEMICAL & ENGINEERING DATA

Article

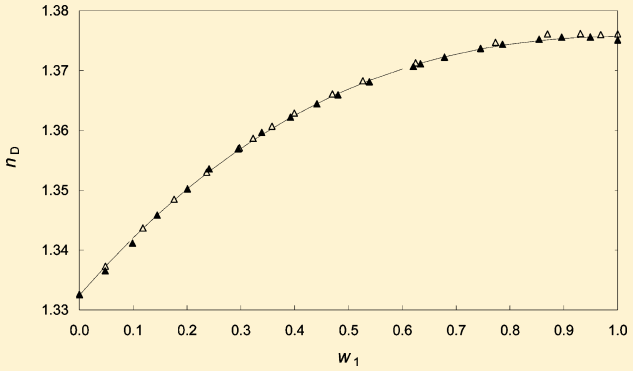
pubs.acs.org/jced

Physical Properties of Binary and Ternary Mixtures of 2-Propanol, Water, and 1-Butyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid

Pablo Navarro, Marcos Larriba, Silvia García, Julián García,* and Francisco Rodríguez

Department of Chemical Engineering, Complutense University of Madrid, E-28040 Madrid, Spain

ABSTRACT: Refractive indices and densities of the 2-propanol + water + 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) ternary system have been measured at 298.15 K. Physical properties of 2-propanol + water and water + [bmim][BF_4] binary mixtures have also been measured at the same temperature, whereas the 2-propanol + [bmim][BF_4] mixture has been measured at 323.15 K, because the total miscibility for this mixture is achieved above this temperature. Molar volume and excess properties have been calculated from the experimental data to analyze the behavior of the mixtures. The refractive index has been correctly adjusted to a third-order polynomial expansion model, whereas density has been adjusted to a second-order equation. Excess molar volumes and refractive index deviations have been successfully fitted to the Redlich−Kister model.



INTRODUCTION

Ionic liquids (ILs) are ionic substances formed by an organic cation and an inorganic anion with a fusion temperature lower than 373.15 K, and a large majority are liquids at ambient temperature.[1] These compounds have very interesting properties that give the possibility of improving processes and decreasing environmental impact. In this way, ILs have low vapor pressure as their principal property from an environmental point of view,[2] and they can be distilled under high vacuum conditions without stability problems.[3] The high-temperature interval operation supported allows applying ILs in different processes.[4] Hence, separation operations are technically easier and emissions are minimized with the use of these compounds. For this reason, ILs are one of the best future alternatives to volatile organic compounds (VOCs) in separation processes.[5−7] As a consequence, in this past decade, research about these ionic substances is increasing significantly.[1]

An azeotropic mixture needs a mass agent to distillate the components involved in it, and ILs are good entrainers to break azeotropes.[8−24] The 2-propanol + water azeotrope has been broken down using ILs as a mass separating agent.[25−30] 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) has been shown to be an effective entrainer for the 2-propanol + water mixture.[27,28] Several authors set physical properties as analysis in some azeotropics systems with the density and refractive index, but 2-propanol, water, and IL ternary system properties have not been measured yet.

Consequently, the aim of this work has been to measure densities and refractive indices of 2-propanol, water, and [bmim][BF_4] ternary system and also to study the corresponding binary mixtures. Deviations from ideality have been studied with a refractive index deviation and excess molar volume to complete this work.

Table 1. Comparison between Experimental and Literature Properties of Pure Substances at 298.15 K: Refractive Index (n_D) and Density (ρ)[a]

	n_D		ρ/g·cm^{-3}	
component	exptl	lit.	exptl	lit.
2-propanol	1.3751	1.37501[31]	0.78082	0.78095[31]
water	1.3325	1.33250[31]	0.99702	0.99704[31]
[bmim][BF_4]	1.4219	1.422[32]	1.20287	1.200297[33]

[a]Standard uncertainties u are $u(n_D)$ = 0.0001 and $u(\rho)$ = 0.00001 g·cm^{-3}.

EXPERIMENTAL SECTION

Anhydrous 2-propanol was supplied by Sigma−Aldrich with a mass fraction greater than 0.999 and a water content lower than 0.0005. Milli-Q water quality was used. The [bmim][BF_4] used was supplied by Iolitec GmbH with purity higher than 0.99 in mass, its specifications being less than 0.00025 and 0.001 in water and halides, respectively. The purity of this IL was analyzed by ^{1}H NMR, and the water content was also determined using the Karl Fischer titration method by the manufacturer. [bmim][BF_4] was stored in a silica gel desiccator to avoid the alteration of its specifications. Physical properties were measured without further purifications.

Received: November 10, 2011
Accepted: February 28, 2012
Published: March 7, 2012

 © 2012 American Chemical Society dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

Table 2. Experimental Refractive Index (n_D) and Calculated Refractive Index Deviation (Δn_D) of 2-Propanol (1) + Water (2) Mixtures at 298.15 K[a]

w_1	n_D	Δn_D
0.0000	1.3325	0.0000
0.0480	1.3365	0.0034
0.0987	1.3412	0.0073
0.1446	1.3458	0.0113
0.2009	1.3502	0.0147
0.2410	1.3536	0.0174
0.2951	1.3569	0.0197
0.3387	1.3597	0.0215
0.3921	1.3622	0.0228
0.4412	1.3645	0.0238
0.4805	1.3660	0.0242
0.5386	1.3681	0.0246
0.6205	1.3707	0.0242
0.6337	1.3711	0.0241
0.6782	1.3722	0.0232
0.7452	1.3737	0.0213
0.7861	1.3744	0.0195
0.8541	1.3752	0.0156
0.8959	1.3756	0.0124
0.9492	1.3756	0.0070
1.0000	1.3751	0.0000

[a]Standard uncertainties u are $u(n_D) = 0.0006$ and $u(\Delta n_D) = 0.001$.

Table 3. Experimental Density (ρ), Calculated Molar Volume (V_m), and Excess Molar Volume (V^E) of 2-Propanol (1) + Water (2) Mixtures at 298.15 K[a]

	ρ	V_m	V^E
w_1	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}
0.0000	0.99702	18.07	0.00
0.0915	0.98205	19.60	−0.19
0.2131	0.96029	22.05	−0.44
0.3299	0.93693	25.00	−0.64
0.4795	0.90669	29.91	−0.90
0.5009	0.90131	30.79	−0.90
0.6180	0.87445	36.32	−0.99
0.6840	0.85873	40.26	−0.98
0.7874	0.83401	48.14	−0.91
0.8788	0.81199	57.68	−0.73
0.8976	0.80744	60.06	−0.67
0.9154	0.80301	62.49	−0.60
0.9311	0.79905	64.78	−0.52
0.9502	0.79422	67.78	−0.42
0.9752	0.78771	72.11	−0.24
0.9895	0.78380	74.84	−0.12
1.0000	0.78082	76.96	0.00

[a]Standard uncertainties u are $u(\rho) = 0.0005$ g·cm^{-3} and $u(V^E) = 0.03$ cm^3·mol^{-1}.

Binary and ternary mixtures were prepared by mass using a Gibertini Crystal 200 precision balance with a precision of ± 1·10^{-4} g. The uncertainty in the mass fraction of the mixtures was estimated to be less than ± 1·10^{-3}. The handling of all mixtures was done in a glovebox filled with dry nitrogen as inert atmosphere to prevent water absorption because 2-propanol and [bmim][BF$_4$] are hygroscopic substances.

Refractive indices were determined using a Rudolph Research Analytical J357 refractometer with a repeatability of ± 4·10^{-5} and temperature precision of ± 0.1 K. The optical wavelength utilized in this work was 589.3 nm corresponding to the Na−D line. The refractometer was calibrated with Milli-Q water quality before all measurements. The uncertainties of the refractive index measurements are indicated along with corresponding experimental data.

Table 4. Experimental Refractive Index (n_D) and Density (ρ) and Calculated Refractive Index Deviation (Δn_D), Molar Volume (V_m), and Excess Molar Volume (V^E) of Water + [bmim][BF$_4$][a] and 2-Propanol + [bmim][BF$_4$][b] Mixtures at (298.15 and 323.15) K, Respectively

			ρ	V_m	V^E
w_1	n_D	Δn_D	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}
Water (1) + [bmim][BF$_4$] (2)					
0.0000	1.4220	0.0000	1.20287	187.91	0.00
0.0098	1.4206	0.0085	1.19953	169.33	0.13
0.0167	1.4194	0.0131	1.19697	158.33	0.23
0.0205	1.4191	0.0157	1.19579	152.83	0.26
0.0290	1.4180	0.0204	1.19314	141.93	0.31
0.0396	1.4169	0.0254	1.18989	130.37	0.35
0.0585	1.4141	0.0313	1.18423	113.89	0.41
0.0982	1.4094	0.0391	1.17348	90.26	0.42
0.1540	1.4033	0.0435	1.15929	70.18	0.39
0.2046	1.3980	0.0444	1.14724	58.60	0.35
0.2517	1.3934	0.0437	1.13664	50.90	0.30
0.3043	1.3883	0.0421	1.12512	44.51	0.26
0.3966	1.3801	0.0380	1.10601	36.63	0.19
0.5061	1.3705	0.0316	1.08429	30.46	0.13
0.6986	1.3549	0.0195	1.04869	23.77	0.06
0.8897	1.3406	0.0072	1.01575	19.74	0.01
1.0000	1.3325	0.0000	0.99702	18.07	0.00
2-Propanol (1) + [bmim][BF$_4$] (2)					
0.0000	1.4155	0.0000	1.1851	190.72	0.00
0.0089	1.4152	0.0015	1.1804	186.91	−0.18
0.0287	1.4143	0.0043	1.1701	179.01	−0.58
0.0624	1.4122	0.0077	1.1474	168.06	−0.35
0.1053	1.4106	0.0120	1.1221	156.07	−0.45
0.1649	1.4077	0.0157	1.0913	142.33	−0.88
0.2183	1.4071	0.0198	1.0618	132.81	−0.78
0.2719	1.4060	0.0226	1.0316	125.15	−0.44
0.3240	1.4030	0.0229	1.0120	117.89	−1.11
0.4108	1.3989	0.0233	0.9733	108.80	−1.19
0.5167	1.3948	0.0234	0.9271	100.47	−0.96
0.5965	1.3910	0.0216	0.9019	94.69	−1.53
0.6194	1.3904	0.0228	0.8888	93.83	−1.04
0.7697	1.3817	0.0172	0.8355	86.56	−0.86
0.8372	1.3749	0.0118	0.8093	84.34	−0.35
0.9344	1.3668	0.0054	0.7787	81.07	−0.18
1.0000	1.3604	0.0000	0.7587	79.21	0.00

[a]Standard uncertainties u are $u(n_D) = 0.0006$, $u(\rho) = 0.0009$ g·cm^{-3}, $u(\Delta n_D) = 0.001$, and $u(V^E) = 0.06$ cm^3·mol^{-1}. [b]Standard uncertainties u are $u(n_D) = 0.001$, $u(\rho) = 0.003$ g·cm^{-3}, $u(\Delta n_D) = 0.002$, and $u(V^E) = 0.3$ cm^3·mol^{-1}.

Densities were determined with an Anton Paar DMA-5000 oscillating U-tube density meter with a repeatability of ± 1·10^{-6} g·cm^{-3} and temperature precision of ± 0.001 K. Milli-Q water was used for the purpose of checking the calibration of the density meter. The viscosity correction of density has been done automatically by the density meter. Density uncertainties are shown in data tables for each mixture studied.

dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

Table 5. Refractive Index (n_D) and Density (ρ) Fitting Parameters (A_{ik}) of 2-Propanol + Water and Water + [bmim][BF_4] Mixtures at 298.15 K and 2-Propanol + [bmim][BF_4] Mixtures at 323.15 K

		order (k)			
property	component (i)	1	2	3	s
	2-Propanol (1) + Water (2)				
n_D	1	1.3886	−0.0227	0.0098	0.0004
	2	1.3716	−0.0307	−0.0084	
ρ/g·cm^{-3}	1	0.8565	−0.0757		0.0006
	2	0.9703	0.0276		
	Water (1) + [bmim][BF_4] (2)				
n_D	1	1.2535	0.2804	−0.2017	0.0002
	2	1.2862	0.3131	−0.1778	
ρ/g·cm^{-3}	1	1.0133	−0.0129		0.0016
	2	1.1188	0.0821		
	2-Propanol (1) + [bmim][BF_4] (2)				
n_D	1	1.5223	−0.4299	0.2673	0.0006
	2	1.5710	−0.4618	0.3062	
ρ/g·cm^{-3}	1	0.7916	−0.0318		0.0036
	2	1.0076	0.1723		

RESULTS AND DISCUSSION

Binary Systems. The refractive index and density have been measured at 298.15 K for 2-propanol + water and water + [bmim][BF_4] mixtures. The refractive index and density of 2-propanol + [bmim][BF_4] have been measured at 323.15 K. As can be seen in Table 1, refractive indices and densities of pure components agree with literature data. Table 2 displays refractive indices of 2-propanol + water, while densities of the same system are shown in Table 3. Refractive indices and densities of water + [bmim][BF_4] and 2-propanol + [bmim]-[BF_4] are shown in Table 4. Both properties have been fitted to a polynomial mass fraction expansion model to get a mathematical relationship between properties and compositions of the mixtures. Fitting lines were calculated using[34]

$$Q = \sum_{k=1}^{K} \sum_{i=1}^{I} A_{ik} \cdot w_i^k \quad (1)$$

where Q is n_D or ρ in g·cm^{-3}, A_{ik} denotes the adjustment coefficients of the model, I denotes the number of components, w_i refers to the mass fraction of the component i, and k is the polynomial degree. The refractive index has been adjusted to a third-order polynomial expansion model, whereas density has been adjusted to a second-order polynomial expansion equation. The standard deviation (s) for each adjustment has been calculated as[35]

$$s = \sqrt{\frac{1}{N-1} \sum_{n=1}^{N} (Q_{exp} - Q_{cal})^2} \quad (2)$$

where Q_{cal} denotes the adjusted property value, Q_{exp} is the experimental property value, and N refers to the number of measurements. Both coefficients and deviations are listed in Table 5.

In Figure 1, a steady increase is shown for the refractive index of the 2-propanol + water subsystem up to a 2-propanol mass fraction of 0.75. Over this value, the refractive index remains almost constant to pure 2-propanol. In the same mixture, density gradually decreases as the 2-propanol fraction grows larger (Figure 2). The refractive index and density of water + [bmim][BF_4] mixtures are also shown in Figures 1 and 2, respectively. The refractive index and density decrease with the increase in water mass fraction. As can be seen graphically, experimental density and refractive index of 2-propanol + water and water + [bmim][BF_4] agree with literature data.[32,33,36]

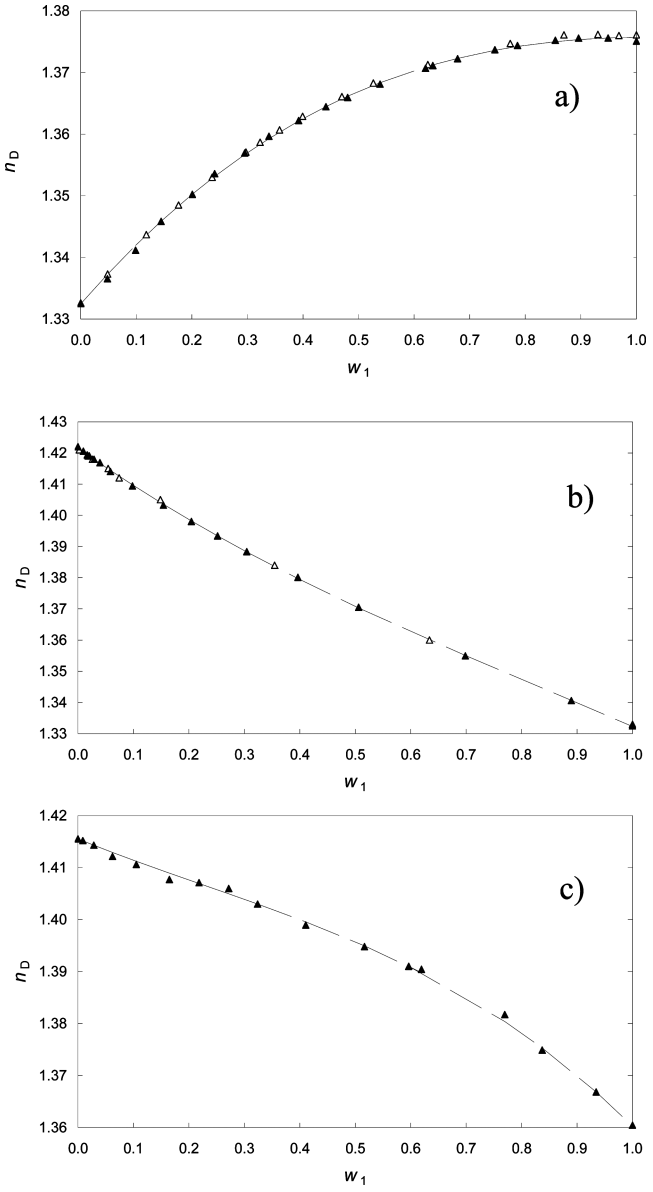


Figure 1. Refractive index (n_D) against the mass fraction of the components: ▲, experimental data; △, literature data.[32,36] Dashed lines are obtained values from fitting to eq 1. (a) 2-Propanol (1) + water (2) at 298.15 K; (b) water (1) + [bmim][BF_4] (2) at 298.15 K; (c) 2-propanol (1) + [bmim][BF_4] (2) at 323.15 K.

To end with binary experimental data, 2-propanol + [bmim]-[BF_4] was measured at 323.15 K. Temperatures over 323.15 K allow total miscibility of both liquids which are not miscible at 298.15 K. Refractive index and density decrease when the mass fraction of 2-propanol in the mixture increases, as it is reflected in Figures 1 and 2, respectively.

A study of ideality of refractive index and density has been done through the calculus of excess properties. The refractive index deviation and excess molar volume have been excess

dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

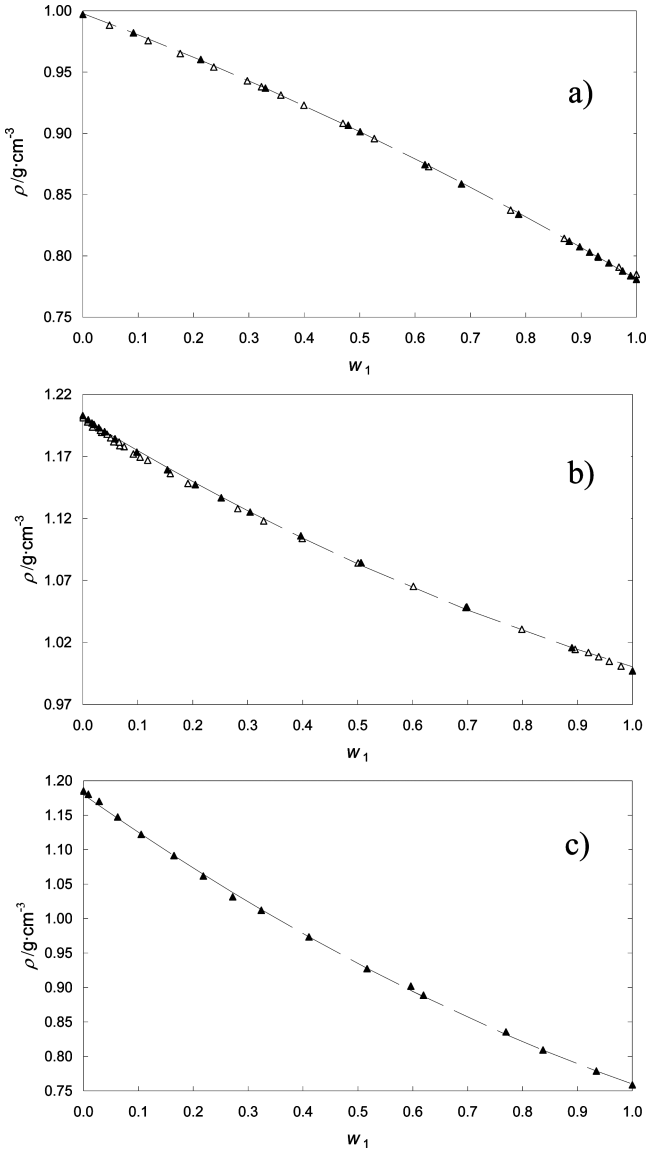


Figure 2. Density (ρ) against mass fraction of the components: ▲, experimental data; △, literature data.[33,36] Dashed lines represent obtained values from fitting to eq 1. (a) 2-Propanol (1) + water (2) at 298.15 K; (b) water (1) + [bmim][BF_4] (2) at 298.15 K; (c) 2-propanol (1) + [bmim][BF_4] (2) at 323.15 K.

Table 6. Refractive Index Deviation (Δn_D) and Excess Molar Volume (V^E) Fitting Parameters (A_k) of 2-Propanol + Water and Water + [bmim][BF_4] Mixtures at 298.15 K and 2-Propanol + [bmim][BF_4] Mixtures at 323.15 K

	order (k)				
excess property	0	1	2	3	s
2-Propanol (1) + Water (2)					
Δn_D	0.0979	0.0136	0.0198	0.0235	0.0004
V^E/ cm^3·mol^{-1}	−3.6159	−1.5668	−1.4936	−3.0721	0.0237
Water (1) + [bmim][BF_4] (2)					
Δn_D	0.1268	−0.0460	0.1973	−0.2900	0.0027
V^E/ cm^3·mol^{-1}	0.5259	0.6137	2.4271	−6.4471	0.0711
2-Propanol (1) + [bmim][BF_4] (2)					
Δn_D	0.0943	−0.0270	0.0211	−0.0069	0.0007
V^E/ cm^3·mol^{-1}	−5.0603	−0.6103	1.2758	2.5510	0.2182

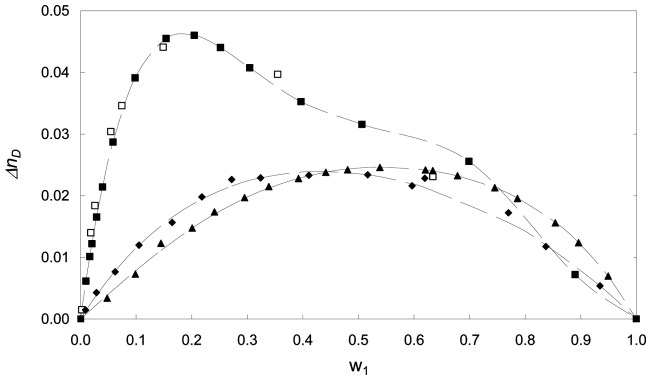


Figure 3. Refractive index deviation (Δn_D): ▲, 2-propanol (1) + water (2) at 298.15 K; ■, water (1) + [bmim][BF_4] (2) at 298.15 K; ◆, 2-propanol (1) + [bmim][BF_4] (2) at 323.15 K. □, water (1) + [bmim][BF_4] (2).[32] Dashed lines are obtained values from fitting to eq 6.

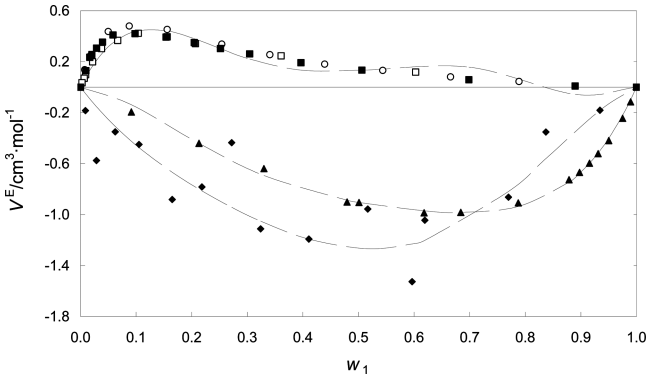


Figure 4. Excess molar volume (V^E): ▲, 2-propanol (1) + water (2) at 298.15 K; ■, water (1) + [bmim][BF_4] (2) at 298.15 K; ◆, 2-propanol (1) + [bmim][BF_4] (2) at 323.15 K. □, water (1) + [bmim][BF_4].[33] ○, water (1) + [bmim][BF_4].[39] Dashed lines refer to obtained values from fitting to eq 6.

properties studied in this work. The refractive index deviation (Δn_D) is defined as[37]

$$\Delta n_D = n_D - \sum_{i=1}^{I} x_i \cdot n_{Di} \tag{3}$$

where n_D is the refractive index of the mixture, x_i denotes the mole fraction of the component i, and n_{Di} indicates the refractive index for each pure component of the mixture.

Excess molar volume (V^E), set as the deviation of ideality of density, is defined following[37]

$$V^E = V_m - \sum_{i=1}^{I} x_i \cdot V_i \tag{4}$$

where V_m is the mixture molar volume, V_i indicates the molar volume for pure component i, and x_i denotes the mole fraction of the component i. Mixture molar volumes were calculated from the experimental densities using[37]

$$V_m = \frac{\sum_{i=1}^{I} W_i \cdot x_i}{\rho} \tag{5}$$

dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

Table 7. Experimental Refractive Index (n_D) and Density (ρ) and Calculated Refractive Index Deviation (Δn_D), Molar Volume (V_m), and Excess Molar Volume (V^E) of the 2-Propanol (1) + Water (2) + [bmim][BF_4] (3) System at 298.15 K[a]

w_1	w_2	n_D	ρ / g·cm^{-3}	Δn_D	V_m / cm^3·mol^{-1}	V^E / cm^3·mol^{-1}
0.0210	0.3882	1.3816	1.1020	0.0389	37.02	0.00
0.0225	0.4948	1.3726	1.0817	0.0332	30.84	−0.06
0.0228	0.6827	1.3577	1.0483	0.0219	24.10	−0.12
0.0254	0.8671	1.3437	1.0102	0.0099	20.19	−0.03
0.0315	0.1981	1.3986	1.1342	0.0442	59.05	0.15
0.0324	0.2944	1.3898	1.1154	0.0427	45.14	0.01
0.0334	0.2433	1.3941	1.1246	0.0437	51.51	0.06
0.0341	0.0161	1.4183	1.1768	0.0152	150.03	0.06
0.0341	0.0565	1.4134	1.1652	0.0312	111.05	0.24
0.0341	0.0949	1.4093	1.1554	0.0387	89.35	0.27
0.0348	0.0382	1.4154	1.1687	0.0254	125.80	0.31
0.0375	0.0094	1.4187	1.1767	0.0110	158.47	0.01
0.0390	0.0197	1.4177	1.1626	0.0175	145.59	1.33
0.0418	0.1476	1.4033	1.1402	0.0427	70.32	0.13
0.0788	0.1282	1.4037	1.1255	0.0403	74.44	−0.02
0.0957	0.0647	1.4095	1.1315	0.0321	99.32	−0.19
0.1023	0.3560	1.3837	1.0735	0.0392	39.04	−0.29
0.1047	0.0244	1.4135	1.1362	0.0207	126.66	−0.36
0.1049	0.4530	1.3760	1.0561	0.0348	32.82	−0.33
0.1088	0.0433	1.4112	1.1292	0.0269	111.15	−0.27
0.1089	0.0258	1.4160	1.1397	0.0242	124.03	−1.03
0.1089	0.6225	1.3630	1.0273	0.0257	25.92	−0.37
0.1124	0.7897	1.3507	0.9998	0.0156	21.68	−0.37
0.1906	0.1495	1.3996	1.0682	0.0395	65.04	−0.46
0.1926	0.3202	1.3852	1.0415	0.0385	41.50	−0.55
0.1946	0.4077	1.3788	1.0279	0.0356	35.21	−0.58
0.1971	0.0795	1.4040	1.0770	0.0324	85.25	−0.47
0.1990	0.5595	1.3679	1.0031	0.0287	28.13	−0.56
0.1999	0.2354	1.3906	1.0487	0.0388	50.47	−0.43
0.2027	0.7093	1.3577	0.9779	0.0211	23.71	−0.50
0.2039	0.0210	1.4088	1.0846	0.0199	115.42	−0.57
0.2074	0.0459	1.4132	1.0624	0.0331	101.18	0.95
0.2082	0.0398	1.4067	1.0754	0.0248	103.28	−0.21
0.2117	0.2289	1.3913	1.0451	0.0390	51.16	−0.48
0.2144	0.3227	1.3798	1.0213	0.0330	41.62	−0.17
0.2176	0.2535	1.3899	1.0411	0.0393	47.95	−0.60
0.2487	0.1734	1.3940	1.0302	0.0367	59.47	−0.13
0.2551	0.1609	1.3952	1.0355	0.0366	61.27	−0.50
0.2598	0.1397	1.3987	1.0322	0.0376	65.76	−0.22
0.2649	0.0996	1.4024	1.0370	0.0355	75.65	−0.24
0.2711	0.2956	1.3849	1.0106	0.0365	43.33	−0.63
0.2887	0.0254	1.4044	1.0452	0.0204	103.47	−0.94
0.3152	0.2716	1.3858	0.9921	0.0359	45.51	−0.52
0.3236	0.3424	1.3809	0.9858	0.0344	39.22	−0.82
0.3265	0.2020	1.3900	1.0009	0.0352	53.34	−0.73
0.3303	0.4678	1.3726	0.9671	0.0304	31.96	−0.81
0.3376	0.5893	1.3643	0.9482	0.0248	27.29	−0.76
0.3542	0.2071	1.3888	0.9879	0.0343	52.36	−0.72
0.3759	0.2674	1.3845	0.9714	0.0340	45.40	−0.74
0.3876	0.0592	1.3974	0.9925	0.0243	82.70	−0.67
0.3969	0.1302	1.3924	0.9807	0.0305	64.03	−0.77
0.3982	0.0350	1.3983	0.9905	0.0201	91.16	−0.60
0.4105	0.2126	1.3869	0.9647	0.0327	51.06	−0.77
0.4318	0.2727	1.3831	0.9498	0.0327	44.56	−0.82
0.4423	0.1492	1.3898	0.9597	0.0300	59.72	−0.79
0.4588	0.2598	1.3826	0.9411	0.0313	45.60	−0.84
0.5058	0.0288	1.3941	0.9483	0.0222	87.33	−0.75
0.5144	0.0249	1.3888	0.9454	0.0306	88.31	−0.75

dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

Table 7. continued

w_1	w_2	n_D	ρ / g·cm^{-3}	Δn_D	V_m / cm^3·mol^{-1}	V^E / cm^3·mol^{-1}
0.5577	0.1042	1.3883	0.9202	0.0238	65.63	−0.79
0.5826	0.3418	1.3744	0.8920	0.0266	38.65	−1.06
0.5974	0.0689	1.3884	0.9087	0.0195	72.21	−0.73
0.6124	0.0472	1.3890	0.9050	0.0168	77.17	−0.68
0.6275	0.2504	1.3773	0.8800	0.0249	45.67	−0.80
0.6863	0.2655	1.3751	0.8630	0.0234	43.94	−1.01
0.6909	0.1747	1.3796	0.8694	0.0222	52.79	−0.99
0.6970	0.1675	1.3793	0.8668	0.0213	53.68	−0.91
0.7588	0.0936	1.3810	0.8510	0.0162	63.60	−0.72
0.7641	0.1822	1.3768	0.8443	0.0199	51.35	−0.93
0.7970	0.0479	1.3816	0.8425	0.0114	71.46	−0.65
0.8316	0.1100	1.3778	0.8279	0.0150	59.79	−0.79
0.8831	0.0549	1.3781	0.8148	0.0095	68.12	−0.57
0.9079	0.0283	1.3780	0.8077	0.0060	72.99	−0.36

[a]Standard uncertainties u are $u(n_D) = 0.0008$, $u(\rho) = 0.001$ g·cm^{-3}, $u(\Delta n_D) = 0.002$, and $u(V^E) = 0.1$ cm^3·mol^{-1}.

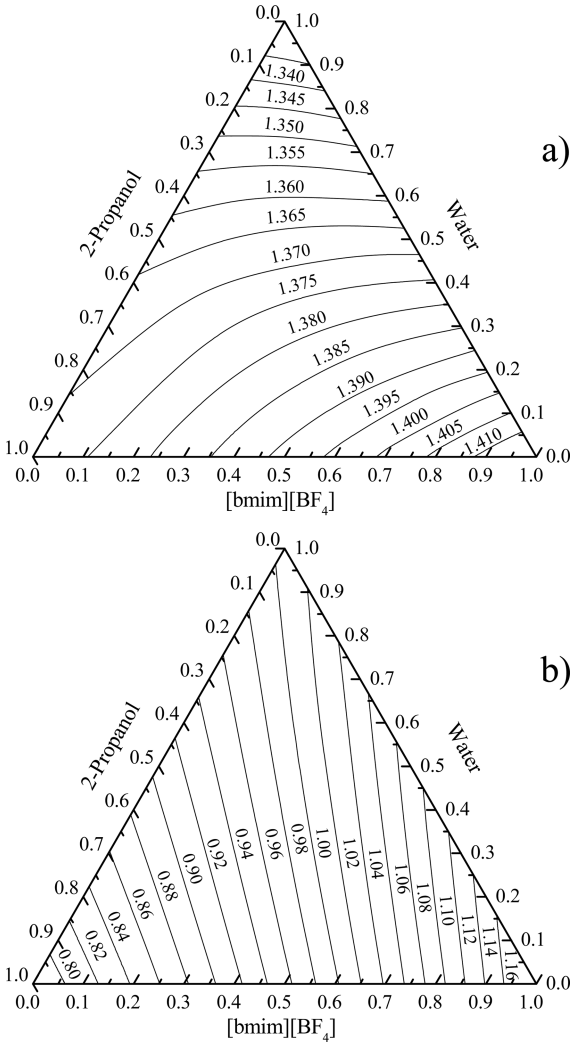


Figure 5. Experimental properties fitting for the 2-propanol + water + [bmim][BF$_4$] system: (a) refractive index and (b) density in g·cm^{-3}.

where W_i is the molecular weight of the pure component i, x_i denotes the mole fraction of the component i, and ρ indicates the experimental density value of the mixture.

Table 8. Refractive Index (n_D) and Density (ρ) Fitting Parameters (A_{ik}) of 2-Propanol (1) + Water (2) + [bmim][BF$_4$] (3) System at 298.15 K

property	component (i)	order (k) 1	2	3	s
n_D	1	1.4201	−0.0700	0.0255	0.0011
	2	1.3540	−0.0221	0.2554	
	3	1.3951	−0.0022	0.0290	
ρ/ g·cm^{-3}	1	0.7559	0.0260		0.0033
	2	1.0777	−0.0713		
	3	1.0829	0.1123		

Table 9. Refractive Index Deviation (Δn_D) and Excess Molar Volume (V^E) Fitting Parameters (A_k) of 2-Propanol + [bmim][BF$_4$] Mixture at 298.15 K

excess property	order (k) 0	1	2	3
Δn_D	0.0802	−0.0027	0.0664	−0.0900
V^E/cm^3·mol^{-1}	−2.3450	4.1025	0.7264	−7.3861

Refractive index deviations and excess molar volumes have been adjusted to the Redlich−Kister model for binary mixtures, corresponding to[38]

$$Q_{ij} = w_i w_j \sum_{k=0}^{K} A_k (2w_i - 1)^k \quad (6)$$

where Q_{ij} denotes the excess property, w_i and w_j are the mass fractions of the components i and j in the binary mixture, and A_k is related to the fitting parameters, k being the order of the fit.

Refractive index deviations, molar volumes, and excess molar volumes are shown in Tables 2, 3, and 4, whereas fitting parameters are shown in Table 6. Both excess properties have been fitted to a third-order model to minimize standard deviation.

In Figures 3 and 4, refractive index deviations and excess molar volumes are shown for 2-propanol + water, water + [bmim][BF$_4$], and 2-propanol + [bmim][BF$_4$] binary systems. Refractive index deviations of all binary mixtures have a positive deviation from ideality. Excess molar volume indicates that

dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

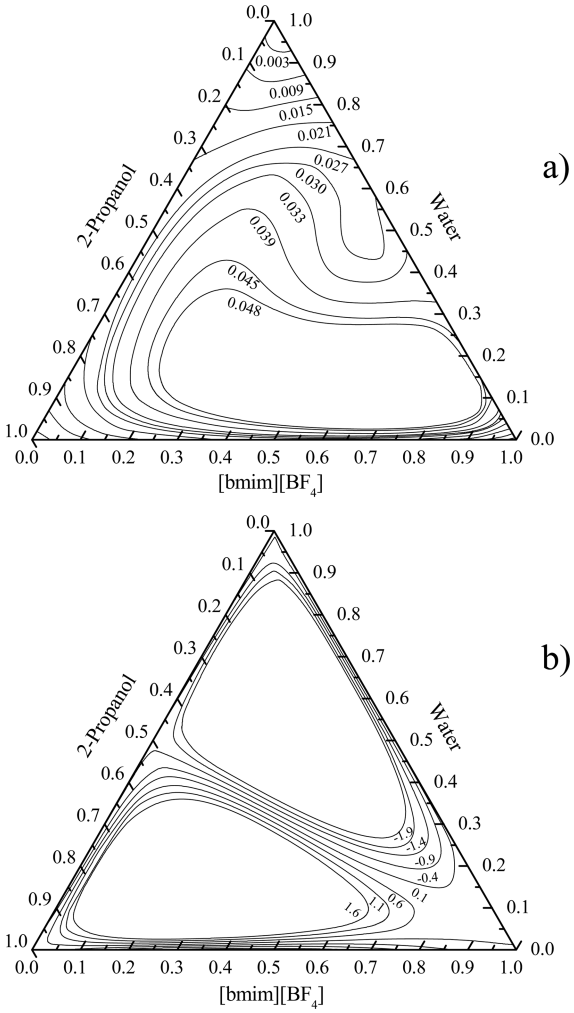


Figure 6. Excess properties fitting for 2-propanol + water + [bmim][BF_4] system: (a) refractive index deviation and (b) excess molar volume, in $cm^3 \cdot mol^{-1}$.

2-propanol + water and 2-propanol + [bmim][BF_4] have a negative deviation from ideality, whereas water + [bmim][BF_4] mixture has a positive one. The excess properties study sets a non-ideal behavior of mixture in the two measured properties.

It is important to underline the comparison between experimental and literature data to the water + [bmim][BF_4] system. Both experimental and literature refractive index deviations present a maximum deviation near to 0.2 water mass fraction.[32] Moreover, the experimental and literature maximum excess volume corresponds to a water mass fraction of 0.1 approximately.[33,39]

The 2-propanol + [bmim][BF_4] mixture has a maximum excess molar volume near to 0.6 2-propanol mass fraction; this value agrees with the alcohol + IL common trend.[40] This phenomenon could be caused by the strong effect of the IL modifying the dielectric constant of the alcohol.[40]

Ternary System. The refractive index and density of the 2-propanol + water + [bmim][BF_4] ternary system were measured at 298.15 K. Experimental properties are reported in Table 7. Experimental data have been adjusted to a model following eq 1 for three components. Hence, isolines have been drawn with the obtained model in Figure 5. Table 8 shows fitting parameters and calculated standard deviation for the ternary system.

An excess properties study has been executed. Refractive index deviation and excess molar volume are the properties analyzed that were calculated with eqs 3 and 4, respectively. Excess properties are also listed in Table 7 and shown in Figure 6. These excess properties have been fitted to a Redlich−Kister ternary third-order model, following[41]

$$Q_{123} = Q_{12} + Q_{13} + Q_{23} + w_1 w_2 w_3 (A + B(w_1 - w_2) + C(w_1 - w_3) + D(w_2 - w_3) + E(w_1 - w_2)^2 + F(w_1 - w_3)^2 + G(w_2 - w_3)^2 + H(w_1 - w_2)^3 + I(w_1 - w_3)^3 + J(w_2 - w_3)^3) \quad (7)$$

where Q_{123} are the ternary excess fitted properties, Q_{12} and Q_{23} refer to the binary fitted properties listed in Table 6 following eq 6, and Q_{13} denote 2-propanol + [bmim][BF_4] parameters at 298.15 K shown in Table 9, whereas w_1, w_2, and w_3 are the mass fractions of the three components involved in the ternary mixtures. Q_{13} have been recalculated because the 2-propanol and [bmim][BF_4] binary system was studied at 323.15 K, and the ternary system requires parameters at 298.15 K. The adjustment coefficients *A*, *B*, *C*, *D*, *E*, *F*, *G*, *H*, *I*, and *J* are shown in Table 10. Both refractive index deviation and excess molar volume indicate the non-ideal trend with composition in ternary 2-propanol + water + [bmim][BF_4] mixtures.

CONCLUSIONS

Refractive indices and densities of 2-propanol + water and water + [bmim][BF_4] binary mixtures over the whole range of compositions have been measured at 298.15 K, whereas these properties for the 2-propanol + [bmim][BF_4] binary system have been measured at 323.15 K. Refractive index deviation and excess molar volume set that both refractive index and density of binary mixtures follow a non-ideal behavior. Moreover, a comparison between experimental and literature properties has shown the reliability of the physical properties obtained.

Refractive indices and densities of 2-propanol + water + [bmim][BF_4] ternary mixtures have been measured at 298.15 K. A study of the behavior of the ternary system has also shown a non-ideal mixing behavior for the studied properties.

Table 10. Refractive Index Deviation (Δn_D) and Excess Molar Volume (V^E) Fitting Parameters of 2-Propanol + Water + [bmim][BF_4] System to the Redlich−Kister Equation at 298.15 K

excess property	*A*	*B*	*C*	*D*	*E*	*F*
Δn_D	0.1018	0.3019	1.3216	−0.2005	−4.3757	−0.7796
$V^E/cm^3 \cdot mol^{-1}$	6.6653	400.0037	429.4725	−441.0718	−56.9452	47.2222
excess property	*G*	*H*	*I*	*J*	*s*	
Δn_D	3.4631	5.4047	−0.9325	−6.4160	0.0061	
$V^E/cm^3 \cdot mol^{-1}$	−84.8700	234.9965	−89.3511	−9.7988	0.3209	

dx.doi.org/10.1021/je201010s | J. Chem. Eng. Data 2012, 57, 1165−1173

AUTHOR INFORMATION

Corresponding Author

*Tel.: +34 91 394 51 19. Fax: +34 91 394 42 43. E-mail address: jgarcia@quim.ucm.es.

Funding

The authors are grateful to the Ministerio de Ciencia e Innovación of Spain (MICINN) and the Comunidad de Madrid for the financial support through projects CTQ2011-23533 and S2009/PPQ-1545, respectively. S.G. also thanks MICINN for awarding her an FPI Grant (reference BES-2009-014703) under the CTQ2008-01591 project.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Rogers, R. D.; Seddon, K. R. Ionic Liquids—Solvents of the Future? *Science* **2003**, *302*, 792−793.

(2) Plechkova, N. V.; Seddon, K. R. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123−150.

(3) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The Distillation and Volatility of Ionic Liquids. *Nature* **2006**, *439*, 831−834.

(4) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of Chloride, Water, and Organic Solvents on the Physical Properties of Ionic Liquids. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(5) DeSimone, J. M. Practical Approaches to Green Solvents. *Science* **2002**, *297*, 799−803.

(6) França, J. M. P.; Nieto de Castro, C. A.; Matos Lopes, M.; Nunes, V. M. B. Influence of Thermophysical Properties of Ionic Liquids in Chemical Process Design. *J. Chem. Eng. Data* **2009**, *54*, 2569−2575.

(7) Seddon, K. R. Ionic Liquids for Clean Technology. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351−356.

(8) Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Zhu, J.; Huang, X. Selection of Ionic Liquids as Entrainers for the Separation of Ethyl Acetate and Ethanol. *Ind. Eng. Chem. Res.* **2009**, *48*, 9006−9012.

(9) Orchillés, A. V.; Miguel, P. J.; Vercher, E.; Martínez-Andreu, A. Ionic Liquids as Entrainers in Extractive Distillation: Isobaric Vapor−Liquid Equilibria for Acetone + Methanol + 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate. *J. Chem. Eng. Data* **2007**, *52*, 141−147.

(10) Zhao, J.; Dong, C.; Li, C.; Meng, H.; Wang, Z. Isobaric Vapor−Liquid Equilibria for Ethanol−Water System Containing Different Ionic Liquids at Atmospheric Pressure. *Fluid Phase Equilib.* **2006**, *242*, 147−153.

(11) Mokhtarani, B.; Gmehling, J. (Vapour + Liquid) Equilibria of Ternary Systems with Ionic Liquids Using Headspace Gas Chromatography. *J. Chem. Thermodyn.* **2010**, *42*, 1036−1038.

(12) Kato, R.; Gmehling, J. Measurement and Correlation of Vapor−Liquid Equilibria of Binary Systems Containing the Ionic Liquids [emim][$(CF_3SO_2)_2N$], [bmim][$(CF_3SO_2)_2N$], [mmim][$(CH_3)_2PO_4$] and Oxygenated Organic Compounds Respectively Water. *Fluid Phase Equilib.* **2005**, *231*, 38−43.

(13) Jork, C.; Seiler, M.; Beste, Y. A.; Arlt, W. Influence of Ionic Liquids on the Phase Behavior of Aqueous Azeotropic Systems. *J. Chem. Eng. Data* **2004**, *49*, 852−857.

(14) Andreatta, A. E.; Arce, A.; Rodil, E.; Soto, A. Physical Properties of Binary and Ternary Mixtures of Ethyl Acetate, Ethanol, and 1-Octyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide at 298.15 K. *J. Chem. Eng. Data* **2009**, *54*, 1022−1028.

(15) Li, Q.; Zhang, J.; Lei, Z.; Zhu, J.; Xing, F. Isobaric Vapor−Liquid Equilibrium for Ethyl Acetate + Ethanol + 1-Ethyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2009**, *54*, 193−197.

(16) Arce, A.; Soto, A.; Ortega, J.; Sabater, G. Viscosities and Volumetric Properties of Binary and Ternary Mixtures of Tris-(2-hydroxyethyl) Methylammonium Methylsulfate + Water + Ethanol at 298.15 K. *J. Chem. Eng. Data* **2008**, *53*, 770−775.

(17) Zhao, J.; Jiang, X.-C.; Li, C.; Wang, Z. Vapor Pressure Measurement for Binary and Ternary Systems Containing a Phosphoric Ionic Liquid. *Fluid Phase Equilib.* **2006**, *247*, 190−198.

(18) Calvar, N.; González, B.; Gómez, E.; Domínguez, A. Vapor−Liquid Equilibria for the Ternary System Ethanol + Water + 1-Butyl-3-methylimidazolium Chloride and the Corresponding Binary Systems at 101.3 kPa. *J. Chem. Eng. Data* **2006**, *51*, 2178−2181.

(19) Wang, J.; Li, C.; Wang, Z. Measurement and Prediction of Vapor Pressure of Binary and Ternary Systems Containing 1-Ethyl-3-methylimidazolium Ethyl Sulfate. *J. Chem. Eng. Data* **2007**, *52*, 1307−1312.

(20) Geng, W.; Zhang, L.; Deng, D.; Ge, Y.; Ji, J. Experimental Measurement and Modeling of Vapor−Liquid Equilibrium for the Ternary System Water + Ethanol + 1-Butyl-3-methylimidazolium Chloride. *J. Chem. Eng. Data* **2010**, *55*, 1679−1683.

(21) Huo, Y.; Xia, S.; Yi, S.; Ma, P. Measurement and Correlation of Vapor Pressure of Benzene and Thiophene with [bmim][PF_6] and [bmim][BF_4] Ionic Liquids. *Fluid Phase Equilib.* **2009**, *276*, 46−52.

(22) Ge, Y.; Zhang, L.; Yuan, X.; Geng, W.; Ji, J. Selection of Ionic Liquids as Entrainers for Separation of (Water + Ethanol). *J. Chem. Thermodyn.* **2008**, *40*, 1248−1252.

(23) Zhao, J.; Li, C.; Wang, Z. Vapor Pressure Measurement and Prediction for Ethanol + Methanol and Ethanol + Water Systems Containing Ionic Liquids. *J. Chem. Eng. Data* **2006**, *51*, 1755−1760.

(24) Çehreli, S.; Gmehling, J. Phase Equilibria for Benzene−Cyclohexene and Activity Coefficients at Infinite Dilution for the Ternary Systems with Ionic Liquids. *Fluid Phase Equilib.* **2010**, *295*, 125−129.

(25) Verma, V. K.; Banerjee, T. Ionic Liquids as Entrainers for Water + Ethanol, Water + 2-Propanol, and Water + THF Systems: A Quantum Chemical Approach. *J. Chem. Thermodyn.* **2010**, *42*, 909−919.

(26) Westerholt, A.; Liebert, V.; Gmehling, J. Influence of Ionic Liquids on the Separation Factor of Three Standard Separation Problems. *Fluid Phase Equilib.* **2009**, *280*, 56−60.

(27) Zhang, L.; Han, J.; Deng, D.; Ji, J. Selection of Ionic Liquids as Entrainers for Separation of Water and 2-Propanol. *Fluid Phase Equilib.* **2007**, *255*, 179−185.

(28) Zhang, L.; Deng, D.; Han, J.; Ji, D.; Ji, J. Isobaric Vapor−Liquid Equilibria for Water + 2-Propanol + 1-Butyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2007**, *52*, 199−205.

(29) Li, Q.; Xing, F.; Lei, Z.; Wang, B.; Chang, Q. Isobaric Vapor−Liquid Equilibrium for Isopropanol + Water + 1-Ethyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2008**, *53*, 275−279.

(30) Döker, M.; Gmehling, J. Measurement and Prediction of Vapor−Liquid Equilibria of Ternary Systems Containing Ionic Liquids. *Fluid Phase Equilib.* **2005**, *227*, 255−266.

(31) Arce, A.; Arce, A. Jr.; Martínez-Ageitos, J.; Rodil, E.; Soto, A. (Vapour + Liquid) Equilibrium of (DIPE + IPA + Water) at 101.32 kPa. *J. Chem. Thermodyn.* **2003**, *35*, 871−884.

(32) Malham, B.; Turmine, M. Viscosities and Refractive Indices of Binary Mixtures of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate with Water at 298 K. *J. Chem. Thermodyn.* **2008**, *40*, 718−723.

(33) Malham, B.; Letellier, P.; Mayaffre, A.; Turmine, M. Part I. Thermodynamic Analysis of Volumetric Properties of Concentrated Aqueous Solutions of 1-Butyl-3-methylimidazolium Tetrafluoroborate, 1-Butyl-2,3-dimethylimidazolium Tetrafluoroborate, and Ethylammonium Nitrate Based on Pseudo-Lattice Theory. *J. Chem. Thermodyn.* **2007**, *39*, 1132−1143.

(34) Calvar, N.; Gonzalez, B.; Domínguez, A.; Tojo, J. Physical Properties of the Ternary Mixture Ethanol + Water + 1-Butyl-3-Methylimidazolium Chloride at 298.15 K. *J. Solution Chem.* **2009**, *35*, 1217−1225.

(35) Andreatta, A. E.; Francisco, M.; Rodil, E.; Soto, A.; Arce, A. Isobaric Vapour−Liquid Equilibria and Physical Properties for Isopropyl Acetate + Isopropanol + 1-Butyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide Mixtures. *Fluid Phase Equilib.* **2011**, *300*, 162−171.

(36) Herráez, J. V.; Belda, R. Refractive Index, Densities and Excess Molar Volumes of Monoalcohols + Water. *J. Solution Chem.* **2006**, *35*, 1315−1328.
(37) Iglesias-Otero, M. A.; Troncoso, J.; Carballo, E.; Romaní, L. Density and Refractive Index in Mixtures of Ionic Liquids and Organic Solvents: Correlations and Predictions. *J. Chem. Thermodyn.* **2008**, *40*, 949−956.
(38) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions. *Ing. Eng. Chem.* **1948**, *40*, 345−348.
(39) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes de Ponte, M.; Szydiovski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romaní, L.; Esperança, J. M. S. S.; Guedes, H. J. R.; Sousa, H. C. A Detailed Thermodynamic Analysis of $[C_4mim][BF_4]$ + Water as a Case Study to Model Ionic Liquid Aqueous Solutions. *Green Chem.* **2004**, *6*, 369−381.
(40) Kurnia, K. A.; Mutalib, M. I. A.; Murugesan, T.; Ariwahjoedi, B. Density and Excess Molar Volume of the Protic Ionic Liquid Bis-(2-hydroxyethyl)ammonium Acetate with Alcohols. *J. Solution Chem.* **2011**, *40*, 470−480.
(41) Arce, A.; Rodil, E.; Soto, A. Volumetric and Viscosity Study for the Mixtures of 2-Ethoxy-2-methylpropane, Ethanol, and 1-Ethyl-3-methylimidazolium Ethyl Sulfate Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 1453−1457.