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Physical Properties of *N*-Butylpyridinium Tetrafluoroborate and *N*-Butylpyridinium Bis(trifluoromethylsulfonyl)imide Binary Ionic Liquid Mixtures

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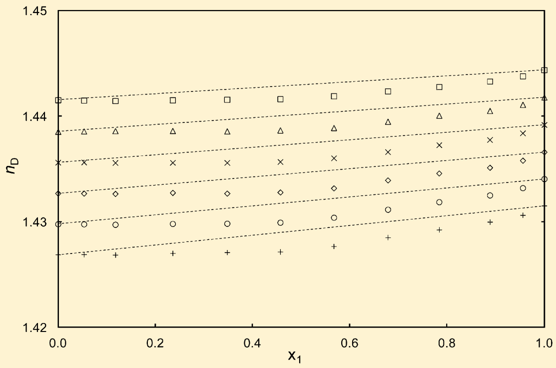

ABSTRACT: The use of the *N*-butylpyridinium tetrafluoroborate ([bpy][BF_4]) + *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide ([bpy][Tf_2N]) binary ionic liquid mixture as an aromatic extraction solvent has recently been proposed. To establish the potential of this mixture to be applied in an aromatic separation process, its physical properties must be measured. In this work, refractive indices, densities, and viscosities of this binary ionic liquid mixture have been determined over the temperature range from (303.15 to 353.15) K at atmospheric pressure. A comparison between the physical properties of the sulfolane and the properties gathered in this work has also been performed. The Bingham mixing rule has successfully estimated the viscosities of the IL mixtures from viscosity data of pure ILs. The accuracy of the group contribution method proposed by Ye and Shreeve and extended by Gardas and Coutinho in predicting densities of pyridinium-based IL mixtures has been studied. Refractive index deviations, excess molar volumes, and viscosity deviations have been correctly fitted to Redlich–Kister polynomial equations.

INTRODUCTION

The potential use of ionic liquids (ILs) as solvents in the liquid–liquid extraction of aromatic hydrocarbons from C_4 to C_{10} aliphatic hydrocarbon mixtures has been widely studied during the last 10 years.[1] As a consequence of its nonvolatile nature, ILs would reduce environmental impact, process steps, and energy consumption of the aromatic separation unit.[1–5]

Sulfolane is the most commonly used solvent in industry into aromatic extraction processes, and for this reason it is employed as a benchmark. A high aromatic distribution ratio and a high separation factor are essential for an IL to be considered as an alternative to sulfolane.[4] However, among pure ILs studied only a small number has shown both a separation factor and an aromatic distribution ratio higher than those of sulfolane.[1]

Fletcher et al. suggested that mixing different ILs in appropriate proportions may have better properties than those of the pure compounds.[6] Therefore, in a previous work,[7] we have investigated *N*-butylpyridinium tetrafluoroborate ([bpy][BF_4]) and *N*-butylpyridinium bis(trifluoromethylsulfonyl)imide ([bpy][Tf_2N]) binary IL mixtures, since the [bpy][BF_4] showed larger separation factor values for aromatics extraction than those of sulfolane,[8] and the [bpy][Tf_2N] presented higher toluene distribution ratios than the sulfolane values.[9] We have concluded that by mixing these two ILs in proper proportions a mixed solvent with better extractive properties than the sulfolane can be obtained.

However, to study the potential of this IL mixture to be applied in an industrial aromatics extraction process, their physical properties must be determined. So far, papers about physical properties of binary IL mixtures are still scarce, and all of them have been focused on imidazolium-based ILs.[10–14] To the best of our knowledge, this work is the first study of the physical properties of binary pyridinium-based IL mixtures.

The aim of this paper has been to measure refractive indices, densities, and viscosities of [bpy][BF_4] + [bpy][Tf_2N] IL mixtures over the whole range of compositions at temperatures between (303.15 and 353.15) K. The temperature range selected covers the common values used in the liquid–liquid extraction of aromatic hydrocarbons with ILs as solvents.[1] Futhermore, a comparison between densities and viscosities of this binary IL mixture and physical properties of the sulfolane has been done. An analysis of the accuracy of the Ye and Shreeve group contribution method[15] in predicting densities of binary pyridinium-based IL mixtures and of the Bingham mixing law[16] in estimating viscosities has also been performed.

EXPERIMENTAL SECTION

[bpy][BF_4] and [bpy][Tf_2N] ILs were supplied by Iolitec GmbH with a mass fraction purity higher than 0.99, which was determined by the manufacturer using NMR analysis. Water and halide mass fractions were lower than 0.0001, being measured by the supplier using Karl Fisher titration and ion chromatography, respectively. ILs were used as received from Iolitec GmbH without further purification processes, and they were kept in their original airtight vessels in a desiccator to prevent water hydration. For the same reason, the handling of

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Table 1. Experimental Refractive Indices (n_D), Densities (ρ), and Dynamic Viscosities (η) of [bpy][BF_4] (1) + [bpy][Tf_2N] (2) IL Mixtures on Mole Fraction (x) as a Function of Temperature[a]

	T/K					
x_1	303.15	313.15	323.15	333.15	343.15	353.15
			n_D			
0.0000	1.4415	1.4386	1.4356	1.4327	1.4298	1.4269
0.0533	1.4415	1.4386	1.4357	1.4327	1.4298	1.4269
0.1178	1.4415	1.4386	1.4356	1.4327	1.4298	1.4269
0.2357	1.4415	1.4386	1.4356	1.4328	1.4298	1.4270
0.3477	1.4416	1.4386	1.4356	1.4327	1.4299	1.4271
0.4571	1.4416	1.4387	1.4357	1.4328	1.4300	1.4272
0.5673	1.4419	1.4389	1.4361	1.4332	1.4304	1.4277
0.6783	1.4424	1.4395	1.4366	1.4340	1.4312	1.4285
0.7838	1.4428	1.4401	1.4373	1.4346	1.4319	1.4293
0.8881	1.4433	1.4405	1.4378	1.4352	1.4325	1.4300
0.9558	1.4438	1.4411	1.4384	1.4358	1.4332	1.4307
1.0000	1.4444	1.4418	1.4392	1.4366	1.4341	1.4315
			ρ/g·cm^{-3}			
0.0000	1.4440	1.4347	1.4254	1.4162	1.4071	1.3980
0.0533	1.4355	1.4263	1.4171	1.4080	1.3989	1.3899
0.1178	1.4249	1.4158	1.4067	1.3977	1.3887	1.3798
0.2357	1.4042	1.3953	1.3864	1.3776	1.3689	1.3601
0.3477	1.3828	1.3742	1.3655	1.3570	1.3484	1.3399
0.4571	1.3601	1.3517	1.3433	1.3350	1.3267	1.3185
0.5673	1.3350	1.3268	1.3188	1.3107	1.3026	1.2947
0.6783	1.3072	1.2994	1.2916	1.2838	1.2761	1.2685
0.7838	1.2780	1.2705	1.2630	1.2555	1.2481	1.2407
0.8881	1.2461	1.2389	1.2317	1.2246	1.2175	1.2104
0.9558	1.2238	1.2168	1.2098	1.2028	1.1959	1.1891
1.0000	1.2103	1.2035	1.1967	1.1899	1.1832	1.1765
			η/mPa·s			
0.0000	49.4	33.8	24.2	17.9	13.7	10.9
0.0533	52.0	35.0	25.0	18.5	14.1	11.1
0.1178	54.1	36.3	25.8	19.2	14.5	11.5
0.2357	58.2	39.1	27.7	20.5	15.5	12.1
0.3477	63.1	42.5	29.8	21.8	16.4	12.8
0.4571	70.2	46.2	31.8	23.1	17.3	13.2
0.5673	75.7	48.4	33.3	23.8	17.6	13.7
0.6783	82.6	53.1	35.7	25.5	18.7	14.4
0.7838	91.2	57.6	38.6	27.3	19.9	15.2
0.8881	105.0	66.2	43.8	30.4	21.9	16.5
0.9558	115.3	70.5	46.1	31.9	22.9	17.1
1.0000	123.6	74.8	48.1	33.0	23.8	17.7

[a] Standard uncertainties u are $u(n_D) = 0.0005$, $u(\rho) = 0.0008$ g·cm^{-3}, $u(\eta) = 1.1$ %.

ILs was performed inside a glovebox under a dry nitrogen atmosphere.

Refractive indices, densities, and dynamic viscosities of the pure or mixed [bpy][BF_4] and [bpy][Tf_2N] ILs were determined at temperatures between (303.15 and 353.15) K. Binary IL mixtures were gravimetrically prepared in tightly closed vials employing a Mettler Toledo AB104 balance with a precision of $\pm 1 \cdot 10^{-4}$ g. Physical properties of the binary mixtures were measured immediately after the mixing process using a Labnet Vortex Mixer. The estimated error in the mole fraction of the binary mixtures was less than 0.0008.

A Rudolph Research Analytical J357 refractometer was used for refractive index measurements with a temperature precision of ± 0.1 K. The uncertainty in refractive index values was estimated to be less than $\pm 5 \cdot 10^{-4}$. The optical wavelength used was 589.3 nm corresponding to the Na–D line, and prior to all measurements, Millipore quality water was employed for the calibration of the refractometer.

Densities of the pure or mixed [bpy][BF_4] and [bpy][Tf_2N] ILs were determined using an Anton Paar DMA-5000 oscillating U-tube density meter. The temperature was measured by two integrated Pt100 probes with a precision of ± 0.01 K. The density meter used an automatic viscosity correction factor. Millipore quality water was employed to check the calibration of the densimeter before each measurement. The uncertainty in density measurements was found to be less than $\pm 8 \cdot 10^{-4}$ g·cm^{-3}.

Dynamic viscosity measurements of the pure compounds and of the binary mixtures were performed using an Anton Paar Automated micro viscometer (AMVn) based on the falling ball principle with a temperature uncertainty of ± 0.01 K. The viscometer was calibrated by the manufacturer using several

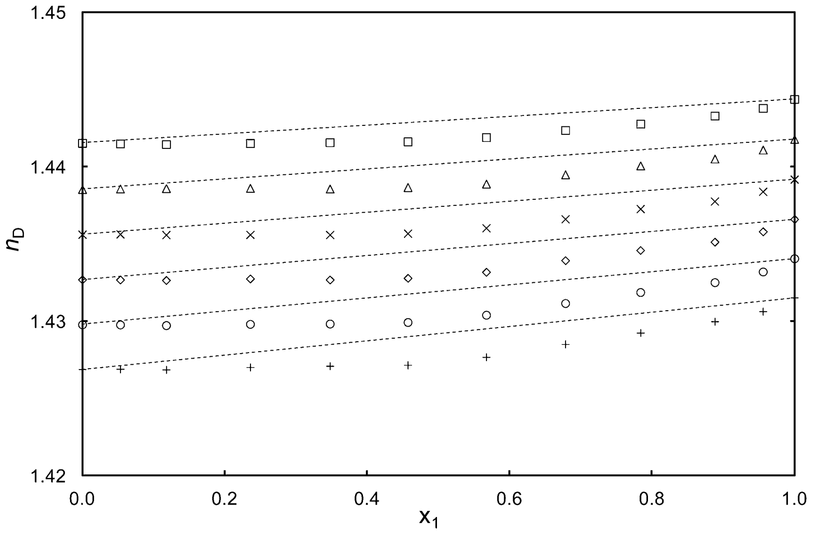

Figure 1. Refractive indices of [bpy][BF_4] (1) + [bpy][Tf_2N] (2) IL mixtures as a function of [bpy][BF_4] mole fraction and temperature: □, 303.15 K; △, 313.15 K; ×, 323.15 K; ◇, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines represent refractive indices of ideal binary mixtures.

viscosity standard fluids. The uncertainty in viscosity measurements was estimated less than ± 1.1 %.

The reliability of the measurement methods was studied in our previous works by comparison between experimental and literature data for different pure ILs.[17−19] To validate the experimental results gathered in this work, we have performed a comparative analysis between experimental and literature properties of the [bpy][BF_4] and [bpy][Tf_2N] pure ILs. The average absolute percent deviation of refractive indices of the [bpy][BF_4] IL was 0.01 %.[20] The average differences between our density data for [bpy][BF_4] and [bpy][Tf_2N] ILs and those from literature were less than 0.17 %.[21−24] Finally, the average percent deviations between experimental and published viscosities of the pure [bpy][BF_4] and [bpy][Tf_2N] ILs were less than 5.95 %.[23,24] These viscosity deviations can be due to the important influence of impurities and water content on the viscosity of ILs.[25]

■ RESULTS AND DISCUSSION

Refractive indices (n_D), densities (ρ), and dynamic viscosities (η) of pure or mixed [bpy][BF_4] and [bpy][Tf_2N] ILs in the whole range of compositions were measured at temperatures between (303.15 and 353.15) K and atmospheric pressure. The experimental data as a function of temperature and the standard uncertainties are listed in Table 1.

Refractive Index. Refractive index values of the [bpy][BF_4] + [bpy][Tf_2N] mixtures are represented in Figure 1. As seen, refractive indices of the IL mixtures decrease as the temperature increases. In Figure 1, dashed lines represent refractive indices of the mixtures estimated using the following ideal mixing rule:

$$n_D = \sum_{i=1}^{2} n_{D,i} x_i \tag{1}$$

where n_D denotes the refractive index of IL mixture, $n_{D,i}$ is the refractive index of the pure IL, and x_i indicates the IL mole fraction in the binary mixture. As can be observed in Figure 1, there are important differences between experimental and ideal refractive indices. This result highlights the non-ideal behavior of the refractive index in the [bpy][BF_4] + [bpy][Tf_2N] IL mixture.

To perform a more detailed analysis of the behavior of refractive index, deviations from ideality (Δn_D) at the temperatures of the measurements are listed in Table 2. Δn_D values have been calculated as the difference between the experimental data and the refractive indices estimated using eq 1. As shown in Figure 2, the largest negative deviations from ideality have been observed at 353.15 K and for [bpy][BF_4] mole fraction close to 0.5. Hence, the behavior of the refractive index of the [bpy][BF_4] + [bpy][Tf_2N] mixture deviates from ideal behavior as temperature increases.

Deviations from ideality of the three physical properties studied have been fitted to Redlich−Kister polynomial equations[26]

$$Q = x_i x_j \sum_{n=0}^{4} A_i (x_i - x_j)^n \tag{2}$$

where Q represents the deviation from ideal mixing behavior of the physical property, A_i are fitting parameters, and n is the polynomial expansion order. A fourth order expansion model has minimized standard deviation of the data fitting. Δn_D values obtained using the Redlich−Kister equation are plotted in Figure 2 as dashed lines along with experimental deviations from ideality. Adjustable parameters and standard deviations of the fits are summarized in Table 3.

Density. Densities of the [bpy][BF_4] + [bpy][Tf_2N] IL mixtures at the measured temperatures are presented in Figure 3. As shown in the graph, density values of the mixtures do not change linearly with the [bpy][BF_4] mole fraction at constant temperature.

Gardas and Coutinho used the group contribution method proposed by Ye and Shreeve[15] to predict accurately densities of binary IL mixtures formed by imidazolium-based ILs.[27] In this work, we have studied the use of this method to estimate densities of pyridinium-based IL mixtures using the following equation:

$$\rho = \frac{\sum_{i=1}^{2} W_i x_i}{N(\sum_{i=1}^{2} V_{0,i} x_i)(a + bT + cP)} \tag{3}$$

Table 2. Refractive Index Deviations (Δn_D), Excess Molar Volumes (V^E), and Dynamic Viscosity Deviations ($\Delta\eta$) of [bpy][BF_4] (1) + [bpy][Tf_2N] (2) IL Mixtures

	T/K					
x_1	303.15	313.15	323.15	333.15	343.15	353.15
			Δn_D			
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0533	−0.0002	−0.0001	−0.0002	−0.0002	−0.0002	−0.0002
0.1178	−0.0004	−0.0003	−0.0004	−0.0005	−0.0006	−0.0006
0.2357	−0.0007	−0.0007	−0.0009	−0.0009	−0.0010	−0.0010
0.3477	−0.0009	−0.0011	−0.0013	−0.0014	−0.0014	−0.0014
0.4571	−0.0012	−0.0014	−0.0016	−0.0017	−0.0018	−0.0018
0.5673	−0.0012	−0.0015	−0.0016	−0.0017	−0.0018	−0.0018
0.6783	−0.0011	−0.0012	−0.0014	−0.0014	−0.0015	−0.0015
0.7838	−0.0010	−0.0010	−0.0011	−0.0012	−0.0013	−0.0013
0.8881	−0.0008	−0.0009	−0.0010	−0.0010	−0.0011	−0.0010
0.9558	−0.0005	−0.0005	−0.0006	−0.0006	−0.0007	−0.0007
1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
			$V^E/cm^3\cdot mol^{-1}$			
0.0000	0.00	0.00	0.00	0.00	0.00	0.00
0.0533	0.07	0.08	0.08	0.09	0.09	0.09
0.1178	0.14	0.15	0.15	0.15	0.16	0.17
0.2357	0.24	0.26	0.26	0.28	0.28	0.29
0.3477	0.33	0.33	0.34	0.35	0.36	0.38
0.4571	0.38	0.38	0.40	0.40	0.41	0.41
0.5673	0.42	0.43	0.44	0.45	0.46	0.47
0.6783	0.44	0.44	0.44	0.45	0.45	0.46
0.7838	0.44	0.45	0.45	0.46	0.47	0.47
0.8881	0.42	0.42	0.43	0.43	0.44	0.44
0.9558	0.35	0.36	0.37	0.38	0.39	0.40
1.0000	0.00	0.00	0.00	0.00	0.00	0.00
			$\Delta\eta$/mPa·s			
0.0000	0.0	0.0	0.0	0.0	0.0	0.0
0.0533	−1.4	−1.0	−0.5	−0.3	−0.1	−0.1
0.1178	−4.1	−2.3	−1.2	−0.6	−0.4	−0.2
0.2357	−8.8	−4.4	−2.2	−1.0	−0.6	−0.3
0.3477	−12.1	−5.6	−2.7	−1.3	−0.9	−0.5
0.4571	−12.6	−6.2	−3.3	−1.8	−1.0	−0.8
0.5673	−15.9	−8.6	−4.4	−2.7	−1.8	−1.1
0.6783	−17.2	−8.5	−4.7	−2.7	−1.9	−1.1
0.7838	−16.4	−8.4	−4.4	−2.4	−1.7	−1.0
0.8881	−10.4	−4.0	−1.6	−0.9	−0.8	−0.4
0.9558	−5.1	−2.5	−1.0	−0.4	−0.5	−0.2
1.0000	0.0	0.0	0.0	0.0	0.0	0.0

where ρ is the density of the binary IL mixture in $kg\cdot m^{-3}$, W_i represents the molecular weight of the pure IL in $kg\cdot mol^{-1}$, N is the Avogadro constant, $V_{0,i}$ indicates the molecular volume of the pure IL assumed as the linear sum of the volumes of anion and cation in $m^3\cdot molecule^{-1}$, T is the temperature in K, and P is the pressure in MPa. The parameters a, b, and c obtained by Gardas and Coutinho were $8.005\cdot10^{-1}$, $6.652\cdot10^{-4}$ K^{-1}, and $-5.919\cdot10^{-4}$ MPa^{-1}, respectively.[27] Volumes of the ions involved in this work were obtained from literature: [bpy] (230 Å^3),[27] [Tf_2N] (248 Å^3),[27] and [BF_4] (73 Å^3).[15]

Densities estimated using this group contribution method are plotted in Figure 3 together with experimental data. The highest accuracy of the method was reached for mixtures with a high content of [bpy][Tf_2N] and at the highest temperatures. The average percent deviation of experimental densities from the estimated densities was 0.35 %. Deviations of the estimations could be due to the influence of impurities on the density, since the method assumes that the IL is composed solely of the anion and the cation, without regard to the volume occupied by impurities. Also keep in mind that the fitting parameters (a, b, and c) were determined by Gardas and Coutinho from densities of imidazolium-based ILs,[27] and in this work we present the densities of a pyridinium-based IL mixture.

A comparison between the density of the {[bpy][BF_4] + [bpy][Tf_2N]} IL mixture and that of sulfolane has been performed. In Figure 3, the density of the sulfolane at 303.15 K is represented as a dotted line.[28] As observed, the density of mixtures with a [bpy][BF_4] mole fraction less than 0.8 is higher than that of sulfolane at 303.15 K. In our recent work, we have concluded that the distribution ratio of toluene and the separation factor were higher than the sulfolane values for a binary IL mixture with a [bpy][BF_4] mole fraction of 0.7.[7] Therefore, the use of this mixture as a solvent would also improve the fluid dynamic behavior and the aromatic extraction efficiency in the extractor, because of its higher density compared to sulfolane.

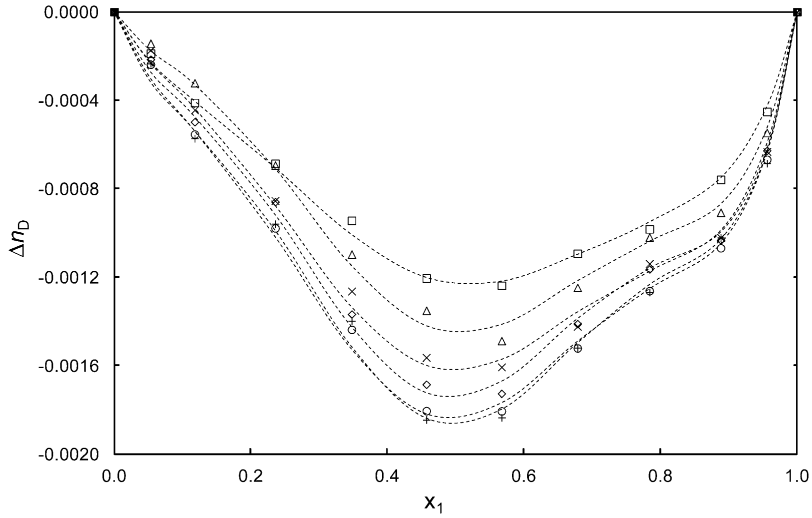

Figure 2. Deviations from ideality of the refractive indices of [bpy][BF_4] (1) + [bpy][Tf_2N] (2) IL mixtures as a function of temperature and composition: □, 303.15 K; △, 313.15 K; ×, 323.15 K; ◇, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines are the fitting curves using Redlich–Kister equations.

Table 3. Fitting Parameters of the Redlich–Kister Polynomial Equation (A_0, A_1, A_2, A_3, A_4) and Standard Deviations (s) for the Excess Properties of [bpy][BF_4] + [bpy][Tf_2N] IL Mixtures at Different Temperatures

T/K	A_0	A_1	A_2	A_3	A_4	s
			Δn_D			
303.15	$-4.92\cdot10^{-3}$	$-6.37\cdot10^{-4}$	$2.83\cdot10^{-3}$	$-2.83\cdot10^{-3}$	$-6.95\cdot10^{-3}$	$3\cdot10^{-5}$
313.15	$-5.81\cdot10^{-3}$	$-3.75\cdot10^{-4}$	$6.08\cdot10^{-3}$	$-5.35\cdot10^{-3}$	$-1.05\cdot10^{-2}$	$4\cdot10^{-5}$
323.15	$-6.49\cdot10^{-3}$	$1.42\cdot10^{-5}$	$5.67\cdot10^{-3}$	$-6.16\cdot10^{-3}$	$-1.10\cdot10^{-2}$	$4\cdot10^{-5}$
333.15	$-6.97\cdot10^{-3}$	$3.42\cdot10^{-4}$	$7.96\cdot10^{-3}$	$-6.36\cdot10^{-3}$	$-1.41\cdot10^{-2}$	$4\cdot10^{-5}$
343.15	$-7.35\cdot10^{-3}$	$3.24\cdot10^{-4}$	$7.14\cdot10^{-3}$	$-6.23\cdot10^{-3}$	$-1.33\cdot10^{-2}$	$4\cdot10^{-5}$
353.15	$-7.47\cdot10^{-3}$	$7.56\cdot10^{-5}$	$8.42\cdot10^{-3}$	$-5.60\cdot10^{-3}$	$-1.49\cdot10^{-2}$	$5\cdot10^{-5}$
			$V^E/\text{cm}^3\cdot\text{mol}^{-1}$			
303.15	1.65	0.28	−0.53	3.01	4.55	0.02
313.15	1.67	0.26	−0.45	3.04	4.55	0.03
323.15	1.71	0.21	−0.54	3.21	4.77	0.03
333.15	1.74	0.20	−0.61	3.23	4.98	0.03
343.15	1.79	0.16	−0.76	3.32	5.32	0.03
353.15	1.82	0.08	−0.61	3.46	5.17	0.03
			$\Delta\eta/\text{mPa}\cdot\text{s}$			
303.15	−57.68	−37.24	−70.91	−4.60	75.48	0.38
313.15	−29.74	−24.95	−25.86	18.35	29.81	0.43
323.15	−15.62	−16.25	−13.96	19.53	22.51	0.23
333.15	−8.87	−11.32	−4.70	14.30	10.07	0.13
343.15	−5.78	−7.94	−3.72	7.97	4.85	0.10
353.15	−3.72	−4.99	0.24	6.05	1.01	0.05

To quantify the deviation of density from ideality, excess molar volumes of the binary mixtures have been calculated at each temperature by using the equation:

$$V^E = \sum_{i=1}^{2} x_i W_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \qquad (4)$$

where V^E is the excess molar volume of the mixture in $\text{cm}^3\cdot\text{mol}^{-1}$, W_i indicates the IL molecular weight in $\text{g}\cdot\text{mol}^{-1}$, ρ is the density of the binary IL mixture in $\text{g}\cdot\text{cm}^{-3}$, and ρ_i represents the density of the pure IL.

Excess molar volumes calculated for {[bpy][BF_4] + [bpy][Tf_2N]} mixtures are listed in Table 2. As seen, excess molar volumes are positive over the whole range of composition, and the highest excess volumes have been obtained in mixtures with a high content of [bpy][BF_4]. In general, molar excess volume increased slightly with temperature at constant composition. The low values of excess molar volumes of the [bpy][BF_4] and [bpy][Tf_2N] mixture are of the same order of magnitude than those obtained by Canongia Lopes et al.,[10] Navia et al.,[11] and Stoppa et al.[13] for binary mixtures composed of 1-alkyl-3-methylimidazolium-based ILs. Therefore, this almost ideal behavior of the pyridinium-based IL mixture studied in this work is similar to that of imidazolium-based IL mixtures.

Excess molar volumes have been fitted to a fourth order Redlich–Kister polynomial expansion (eq 2). Calculated excess molar volumes are presented as dashed lines in Figure 4 together with experimental data. Fitting parameters and standard deviations at different temperatures are summarized in Table 3.

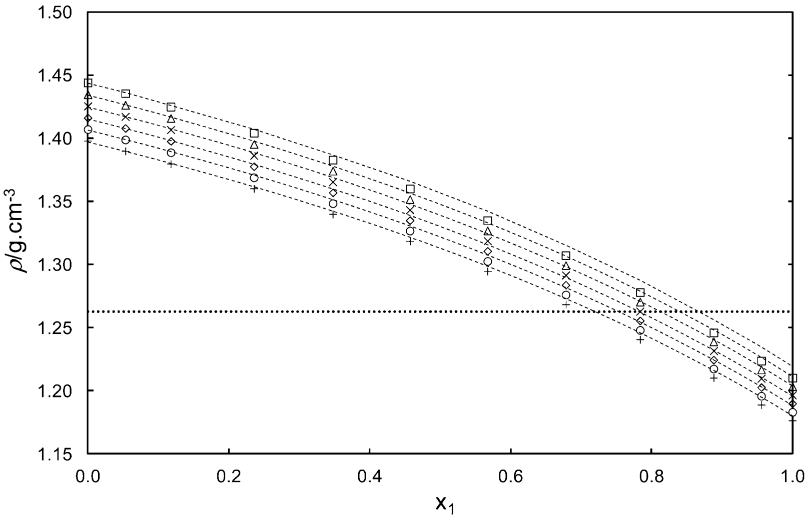

Figure 3. Densities of [bpy][BF$_4$] (1) + [bpy][Tf$_2$N] (2) IL mixtures at different temperatures and compositions: □, 303.15 K; △, 313.15 K; ×, 323.15 K; ◇, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines represent densities estimated from the group contribution model proposed by Ye and Shreeve and extended by Gardas and Coutinho, and the dotted line denotes the density of sulfolane at 303.15 K (from ref 28).

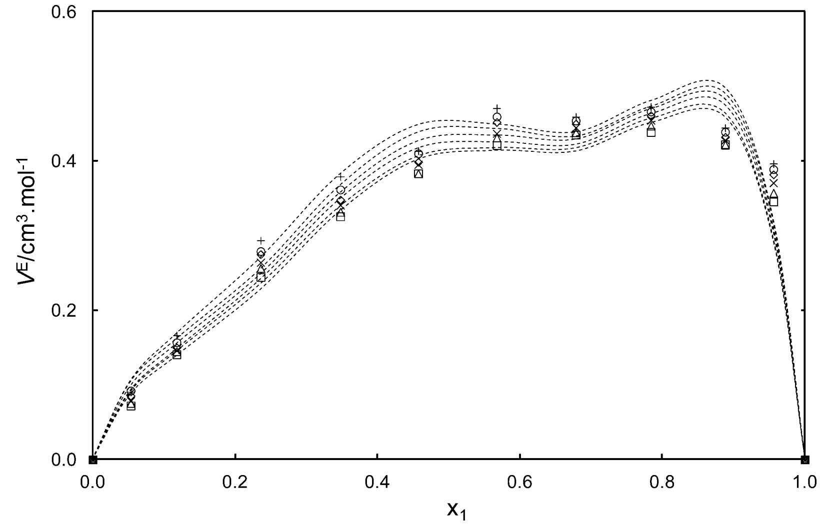

Figure 4. Excess molar volumes for [bpy][BF$_4$] (1) + [bpy][Tf$_2$N] (2) IL mixtures as a function of temperature: □, 303.15 K; △, 313.15 K; ×, 323.15 K; ◇, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines are the fitting curves using Redlich−Kister polynomial equations.

Viscosity. Experimental dynamic viscosities of [bpy][BF$_4$] + [bpy][Tf$_2$N] IL mixtures at the temperature range of (303.15 to 353.15) K are graphically shown in Figure 5. Stoppa et al. in their study about the ideality of binary mixtures of imidazolium-based ILs used the Bingham mixing rule to predict correctly viscosities of IL mixtures from viscosity data for pure ILs:[13,16]

$$\frac{1}{\eta} = \sum_{i=1}^{2} \frac{x_i}{\eta_i} \tag{5}$$

where η is the dynamic viscosity of the binary IL mixture and η_i denotes the viscosity of the pure IL. Viscosities estimated using eq 5 are represented in Figure 5 along with experimental data. The average percent deviation between experimental and predicted viscosities was 1.32 %. Therefore, the Bingham equation seems accurate enough to estimate viscosities of binary IL mixtures from viscosity data of pure pyridinium-based ILs.

In extraction processes, a low viscosity is a favorable property of a solvent as a result of the reduction of pumping and mixing costs.[1] For this reason, a comparative study between the viscosity of the sulfolane[28] and the viscosity values of the [bpy][BF$_4$] + [bpy][Tf$_2$N] IL mixtures at 303.15 K has also been performed in Figure 5. Viscosities of the binary mixtures over the whole range of composition are significantly higher than that of sulfolane. Therefore, this could be a significant drawback in the use of this binary IL mixture as aromatic extraction solvent in the industrial scale.

Deviations from ideality of the viscosity ($\Delta\eta$) of the IL mixtures have been estimated as follows:

$$\Delta\eta = \eta - \sum x_i \eta_i \tag{6}$$

$\Delta\eta$ values of the {[bpy][BF$_4$] + [bpy][Tf$_2$N]} mixtures are summarized in Table 2. Viscosity deviation values have been correctly fitted to a fourth-order Redlich−Kister polynomial expansion (eq 2) as seen in Figure 6. Fitting parameters and standard deviations of the Redlich−Kister model are listed in

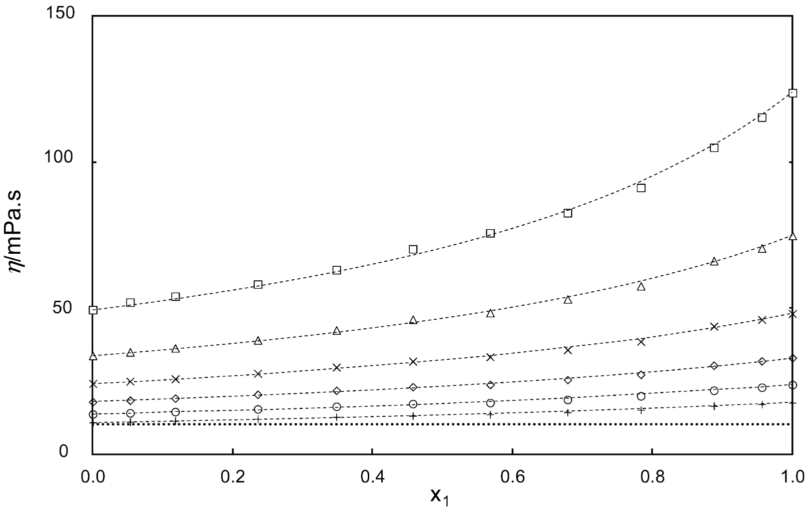

Figure 5. Dynamic viscosities of [bpy][BF_4] (1) + [bpy][Tf_2N] (2) IL mixtures as a function of [bpy][BF_4] mole fraction and temperature: □, 303.15 K; △, 313.15 K; ×, 323.15 K; ◇, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines represent the viscosities calculated with Bingham mixing law, and the dotted line denotes the viscosity of sulfolane at 303.15 K (from ref 28).

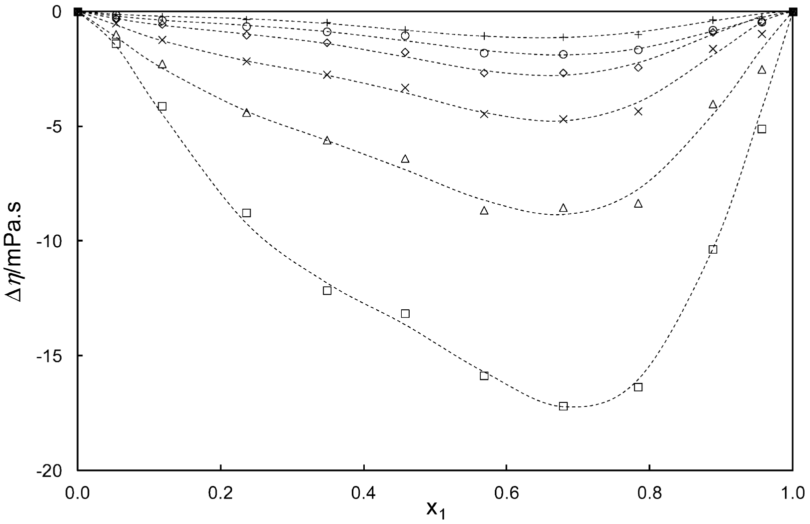

Figure 6. Deviations from ideality of the dynamic viscosities of [bpy][BF_4] (1) + [bpy][Tf_2N] (2) IL mixtures at different temperatures: □, 303.15 K; △, 313.15 K; ×, 323.15 K; ◇, 333.15 K; ○, 343.15 K; +, 353.15 K. Dashed lines are the fitting curves using Redlich−Kister polynomial expansions.

Table 3. All mixtures have shown negative viscosity deviations from ideality, becoming more negative as the temperature decreases. $\Delta\eta$ absolute values are the same order of magnitude than those for {[bmim][BF_4] + [bmim][PF_6]} and {[hmim]-[BF_4] + [hmim][PF_6]} binary IL mixtures obtained by Khupse et al. at different temperatures.[14]

■ CONCLUSIONS

Refractive indices, densities, and viscosities of {[bpy][BF_4] + [bpy][Tf_2N]} IL mixtures have been measured from (303.15 to 353.15) K at atmospheric pressure. The use of binary mixtures with a [bpy][BF_4] mole fraction less than 0.8 could improve the aromatic extraction efficiency because of its higher density compared to sulfolane. On the other hand, this mixture has exhibited viscosities substantially higher than that of sulfolane, which may limit its use as an alternative solvent in the liquid−liquid extraction of aromatic hydrocarbons.

Experimental viscosities have been accurately predicted by the Bingham mixing rule, whereas the group contribution method proposed by Ye and Shreeve and extended by Gardas and Coutinho has been used to accurately estimate densities of mixtures rich in [bpy][Tf_2N].

The analysis of the excess properties has allowed us to study the behavior of this binary IL mixture at different temperatures. The low values of excess volumes obtained have shown the almost ideal behavior of the density. Refractive index deviations from ideality have become larger as the temperature increases, whereas the effect of temperature on viscosity deviations has been the opposite.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Meindersma, G. W.; Hansmeier, A. R.; de Haan, A. B. Ionic Liquids for Aromatics Extraction. Present Status and Future Outlook. *Ind. Eng. Chem. Res.* **2010**, *49*, 7530−7540.

(2) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. L. Liquid−Liquid Equilibria for Toluene + Heptane + 1-Ethyl-3-methylimidazolium Triiodide and Toluene + Heptane + 1-Butyl-3-methylimidazolium Triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.

(3) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Selection of Ionic Liquids for the Extraction of Aromatic Hydrocarbons from Aromatic/aliphatic Mixtures. *Fuel Process. Technol.* **2005**, *87*, 59−70.

(4) Meindersma, G. W.; de Haan, A. B. Conceptual Process Design for Aromatic/aliphatic Separation with Ionic Liquids. *Chem. Eng. Res. Des.* **2008**, *86*, 745−752.

(5) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for "Clean" Liquid−Liquid Extraction. *Chem. Commun.* **1998**, *16*, 1765−1766.

(6) Fletcher, K. A.; Baker, S. N.; Baker, G. A.; Pandey, S. Probing Solute and Solvent Interactions within Binary Ionic Liquid Mixtures. *New J. Chem.* **2003**, *27*, 1706−1712.

(7) García, S.; Larriba, M.; García, J.; Torrecilla, J. S.; Rodríguez, F. Liquid−liquid Extraction of Toluene from Heptane Using Binary Mixtures of *N*-butylpyridinium Tetrafluoroborate and *N*-butylpyridinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids. *Chem. Eng. J.* **2012**, *180*, 210−215.

(8) García, J.; García, S.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Liquid-liquid Equilibria for the Ternary Systems {Heptane + Toluene + *N*-Butylpyridinium Tetrafluoroborate or *N*-Hexylpyridinium Tetrafluoroborate} at $T = 313.2$ K. *J. Chem. Eng. Data* **2010**, *55*, 2862−2865.

(9) García, J.; García, S.; Torrecilla, J. S.; Rodríguez, F. N-butylpyridinium Bis-(trifluoromethylsulfonyl)imide Ionic Liquids as Solvents for the Liquid−liquid Extraction of Aromatics from Their Mixtures with Alkanes: Isomeric Effect of the Cation. *Fluid Phase Equilib.* **2011**, *301*, 62−66.

(10) Canongia Lopes, J. N.; Cordeiro, T. C.; Esperança, J. M. S. S.; Guedes, H. J. R.; Huq, S.; Rebelo, L. P. N.; Seddon, K. R. Deviations from Ideality in Mixtures of Two Ionic Liquids Containing a Common Ion. *J. Phys. Chem. B* **2005**, *109*, 3519−3525.

(11) Navia, P.; Troncoso, J.; Romaní, L. Excess Magnitudes for Ionic Liquid Binary Mixtures with a Common Ion. *J. Chem. Eng. Data* **2007**, *52*, 1369−1374.

(12) Navia, P.; Troncoso, J.; Romaní, L. Viscosities for Ionic Liquid Binary Mixtures with a Common Ion. *J. Solution Chem.* **2008**, *37*, 677−688.

(13) Stoppa, A.; Buchner, R.; Hefter, G. How Ideal Are Binary Mixtures of Room-Temperature Ionic Liquids? *J. Mol. Liq.* **2010**, *153*, 46−51.

(14) Khupse, N. D.; Kurolikar, S. R.; Kumar, A. Temperature Dependent Viscosity of Mixtures of Ionic Liquids at Different Compositions. *Indian J. Chem.* **2010**, *49A*, 727−730.

(15) Ye, C.; Shreeve, J. M. Rapid and Accurate Estimation of Densities of Room-Temperature Ionic Liquids and Salts. *J. Phys. Chem. A* **2007**, *111*, 1456−1461.

(16) Bingham, E. C. *Fluidity and Plasticity*; McGraw-Hill: New York, 1922.

(17) Fernández, A.; García, J.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Volumetric, Transport and Surface Properties of [bmim][$MeSO_4$] and [emim][$EtSO_4$] Ionic Liquids As a Function of Temperature. *J. Chem. Eng. Data* **2008**, *53*, 1518−1522.

(18) Torrecilla, J. S.; Palomar, J.; García, J.; Rodríguez, F. Effect of Cationic and Anionic Chain Lengths on Volumetric, Transport, and Surface Properties of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids at (298.15 and 313.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1297−1301.

(19) Larriba, M.; García, S.; García, J.; Torrecilla, J. S.; Rodríguez, F. Thermophysical Properties of 1-Ethyl-3-methylimidazolium 1,1,2,2-Tetrafluoroethanesulfonate and 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquids as a Function of Temperature. *J. Chem. Eng. Data* **2011**, *56*, 3589−3597.

(20) Bandrés, I.; Royo, F. M.; Gascón, I.; Castro, M.; Lafuente, C. Anion Influence on Thermophysical Properties of Ionic Liquids: 1-Butylpyridinium Tetrafluoroborate and 1-Butylpyridinium Triflate. *J. Phys. Chem. B* **2010**, *114*, 3601−3607.

(21) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Phase Behavior of Ionic Liquid/CO_2 Systems. *J. Phys. Chem. B* **2001**, *105*, 2437−2444.

(22) Gu, Z.; Brennecke, J. F. Volume Expansivities and Isothermal Compressibilities of Imidazolium and Pyridinium-based Ionic Liquids. *J. Chem. Eng. Data* **2002**, *47*, 339−345.

(23) Mokhtarani, B.; Sharifi, A.; Mortaheb, H. R.; Mirzaei, M.; Mafi, M.; Sadeghian, F. Density and Viscosity of Pyridinium-based Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures. *J. Chem. Thermodyn.* **2009**, *41*, 323−329.

(24) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. How Ionic Are Room-Temperature Ionic Liquids? An Indicator of the Physicochemical Properties. *J. Phys. Chem. B* **2006**, *110*, 19593−19600.

(25) 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.

(26) Redlich, O.; Kister, A. T. Thermodynamics of Non Electrolyte Solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(27) Gardas, R. L.; Coutinho, J. A. P. Extension of the Ye and Shreeve Group Contribution Method for Density Estimation of Ionic Liquids in a Wide Range of Temperatures and Pressures. *Fluid Phase Equilib.* **2008**, *263*, 26−32.

(28) Kelayeh, S. A.; Jalili, A. H.; Ghotbi, C.; Hosseini-Jenab, M.; Taghikhani, V. Densities, Viscosities, and Surface Tensions of Aqueous Mixtures of Sulfolane + Triethanolamine and Sulfolane + Diisopropanolamine. *J. Chem. Eng. Data* **2011**, *56*, 4317−4324.