

# Synthesis and Physical Properties of 1-Ethyl 3-methylpyridinium Ethylsulfate and Its Binary Mixtures with Ethanol and Water at Several Temperatures

Begoña González,<sup>†</sup> Noelia Calvar,<sup>†</sup> Elena Gómez,<sup>†</sup> Eugénia A. Macedo,<sup>‡</sup> and Ángeles Domínguez<sup>\*†</sup>

Departamento de Ingeniería Química de la Universidad de Vigo, 36310 Vigo, Spain, and Laboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

In this paper, the ionic liquid [empy][EtSO<sub>4</sub>] was synthesized, and its experimental densities, dynamic viscosities, and refractive indices were determined from (298.15 to 343.15) K. Densities and dynamic viscosities for [empy][EtSO<sub>4</sub>] + ethanol and + water at temperatures  $T = (298.15, 313.15, \text{ and } 328.15)$  K have been measured over the whole composition range and at 0.1 MPa. The determined physical properties have never been reported. Excess molar volumes and viscosity deviations for the binary systems at the above-mentioned temperatures were calculated and fitted to the Redlich–Kister equation. Refractive indices were measured at 298.15 K over the whole composition range for ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2) binary systems. The results were used to calculate deviations in the refractive index.

## Introduction

Ionic liquids (ILs) are room temperature molten salts with unusual properties, such as their very low vapor pressures. This and other properties, such as their ability to solubilize an enormous variety of compounds, good thermal stability which make them liquid over a large temperature range including ambient temperature, nonflammability, and facility to recycle, make the ILs a new alternative of solvents for different processes. The use of ILs in separation processes is one of the multiple alternatives. Nowadays, these salts have attracted worldwide scientific interest in academia and industry.

ILs are tuneable, and there are many possible ionic liquids by combination of cations and anions.<sup>1</sup> To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties including viscosity and density. The most studied ILs are those containing ammonium and imidazolium cations. Nevertheless, there are few investigations on ILs containing pyridinium cations.<sup>2–5</sup> In this work, we report three key thermophysical properties, density, refractive index, and viscosity, of the ionic liquid 1-ethyl 3-methylpyridinium ethylsulfate, [empy][EtSO<sub>4</sub>]. This is a relatively new ionic liquid, and little information about its physical properties is available in the literature.<sup>2</sup>

As an extension of our work concerning dynamic viscosity of binary systems and synthesis of ionic liquids,<sup>6,7</sup> in this paper, experimental density, refractive index, and dynamic viscosity of pure [empy][EtSO<sub>4</sub>] have been measured from  $T = (298.15 \text{ to } 343.15)$  K. Experimental density data were used to calculate the coefficient of thermal expansion. Experimental density and dynamic viscosity data over the whole composition range for binary systems ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2) have been determined at temperatures  $T = (298.15, 313.15, \text{ and } 328.15)$  K at atmospheric pressure.

The results were used to calculate excess molar volumes and viscosity deviations. Refractive indices were measured at 298.15 K over the whole composition range for ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2). The results were used to calculate deviations in the refractive index. The binary mixtures of this ionic liquid with ethanol and water were chosen for a later study about the usefulness of ILs as separation agents for the azeotropic mixture ethanol + water. No literature data for [empy][EtSO<sub>4</sub>] mixtures were found.

## Experimental

**Chemicals.** Ethanol was supplied by Merck with a purity higher than 99.8 %. It was degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere. The mass fraction of water was less than  $10^{-4}$ , determined using a 756 Karl Fisher coulometer. Water was bidistilled.

**Synthesis of 1-Ethyl-3-methylpyridinium Ethylsulfate.** The ionic liquid used in this work was synthesized in our laboratory following the standard synthesis for other sulfate ionic liquids, as published elsewhere.<sup>8</sup> The ionic liquid obtained was dried by heating to (343.15 to 353.15) K and stirring under high vacuum ( $2 \cdot 10^{-1}$  Pa) for 48 h. To ensure its purity, a NMR was made: <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, ppm) 9.07 [s, 1H, H-2], 9.01 [d, 1H,  $J = 6.0$  Hz, H-6], 8.21 [d, 1H,  $J = 8.0$  Hz, H-4], 7.96 [dd, 1H,  $J = 6.4$  y 7.6 Hz, H-5], 4.81 [dd, 2H,  $J = 7.3$  Hz, H-7], 4.09 [dd, 2H,  $J = 7.1$  Hz, H-10], 2.62 [s, 3H, H-9], 1.66 [t, 3H,  $J = 7.3$  Hz, H-8], 1.28 [t, 3H,  $J = 7.1$  Hz, H-11].

The ionic liquid was kept in bottles with inert gas. To remove organic solvents and water content to negligible values (mass fraction of water less than  $7 \cdot 10^{-4}$  determined using a 756 Karl Fisher coulometer), a vacuum ( $2 \cdot 10^{-1}$  Pa) and moderate temperature (343.15 K) were applied to the IL for several days, always immediately prior to their use.

Table 1 shows a comparison between experimental and literature data of the pure components at 298.15 K. Compared

\* To whom correspondence should be addressed. E-mail: admiguez@uvigo.es. Tel.: +34 986 812 422. Fax: +34 986 812 382.

<sup>†</sup> Departamento de Ingeniería Química de la Universidad de Vigo.

<sup>‡</sup> Faculdade de Engenharia da Universidade do Porto.

**Table 1. Comparison of Measured Pure Component Property Data with Literature Values at  $T = 298.15$  K**

component	$\rho/\text{g}\cdot\text{cm}^{-3}$		$n_D$		$10^3\eta/\text{Pa}\cdot\text{s}$	
	exptl	lit. <sup>a</sup>	exptl	lit. <sup>a</sup>	exptl	lit.
ethanol	0.78546	0.7854 <sup>b</sup>	1.35920	1.35941 <sup>c</sup>	1.082	1.082 <sup>b</sup>
water	0.99705	0.99705 <sup>c</sup>	1.33251	1.3325029 <sup>c</sup>	0.890	0.89025 <sup>c</sup>
[empy] [EtSO <sub>4</sub> ]	1.22226	n.a.	1.50666	n.a.	161.4	150 <sup>d</sup>

<sup>a</sup> n.a.: not available. <sup>b</sup> From ref 9. <sup>c</sup> From ref 10. <sup>d</sup> From ref 2.

**Table 2. Density,  $\rho$ , Refractive Index,  $n_D$ , and Dynamic Viscosity,  $\eta$ , of [empy][EtSO<sub>4</sub>] at Several Temperatures**

$T/\text{K}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	$n_D$	$10^3\eta/\text{Pa}\cdot\text{s}$
298.15	1.22226	1.50666	161.4
303.15	1.21902	1.50525	123.6
308.15	1.21578	1.50386	96.9
313.15	1.21254	1.50246	77.1
318.15	1.20939	1.50106	62.2
323.15	1.20613	1.49965	50.55
328.15	1.20286	1.49825	42.32
333.15	1.19963	1.49683	35.52
338.15	1.19643	1.49540	30.11
343.15	1.19325	1.49361	25.69

**Table 3. Fitting Parameters of Equations 1 and 2 together with the Deviations of the Fit (rmsd) for the Density and Refractive Index of [empy][EtSO<sub>4</sub>]**

physical properties	$a$	$b$	$c$	rmsd/ $\text{g}\cdot\text{cm}^{-3}$
$\rho$	1.4188	$-6.7\cdot 10^{-4}$	$-2.9\cdot 10^{-8}$	$3.14\cdot 10^{-5}$
physical properties	$d$	$e$	rmsd	
$n_D$	1.5918	$-2.9\cdot 10^{-4}$	$1.15\cdot 10^{-5}$	

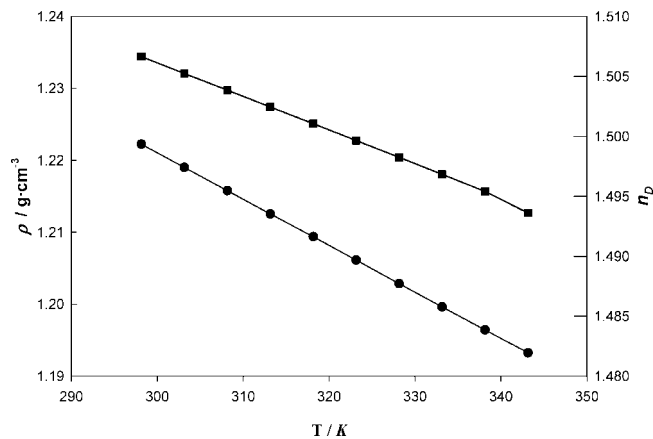
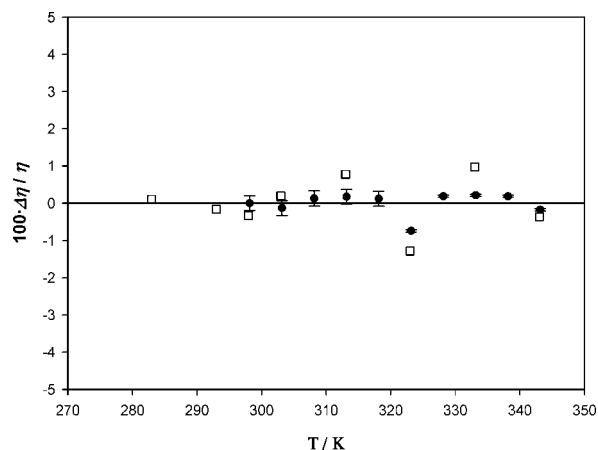
**Table 4. Adjustable Parameters of the VFT Equation ( $A$ ,  $k$ , and  $T_0$ ) together with the Deviation of the Fit (rmsd) for the Viscosity of Pure [empy][EtSO<sub>4</sub>]**

equation	$A/\text{mPa}\cdot\text{s}\cdot\text{K}$	$k/\text{K}$	$T_0/\text{K}$	rmsd
VFT	$5.1\cdot 10^{-3}$	991	166	0.0028

to the literature, the viscosity values for pure [empy][EtSO<sub>4</sub>] are higher than those reported by Crosthwaite et al.<sup>2</sup> The small differences are due to the water content of ionic liquid ( $w = 6.6\cdot 10^{-4}$  for our samples and  $2.56\cdot 10^{-4}$  for Crosthwaite samples) or nonvolatile impurities in their samples or our samples.

**Apparatus and Procedure.** Samples were prepared by syringing known masses of the pure liquids into stoppered bottles, in an inert-atmosphere glovebox. For weight measurements, a Mettler AX-205 Delta Range balance with a precision of  $\pm 10^{-5}$  g was used. A glovebox was used because the ionic liquid is moisture sensitive. Good mixing was ensured by magnetic stirring. All samples were prepared immediately prior to measurements to avoid variations in composition due to evaporation of solvent or pickup of water by the hygroscopic IL.

Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with four Ubbelohde capillary microviscosimeters of  $0.4\cdot 10^{-3}$  m,  $0.53\cdot 10^{-3}$  m,  $0.70\cdot 10^{-3}$  m, and  $1.26\cdot 10^{-3}$  m diameter (the uncertainty in experimental measurement is ( $\pm 0.001$ ,  $\pm 0.01$ ,  $\pm 0.03$ , and  $\pm 0.2$ ) mPa·s, respectively). Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary is maintained in a D20KP LAUDA thermostat with an uncertainty of 0.01 K. The capillaries are calibrated and credited by the company. The equipment has a control unit PVS1 (Processor Viscosity System) that is a PC-controlled instrument for the precise measurement of the fall time, using standardized glass capillaries, with an

**Figure 1.** Plot of experimental values of ●, densities,  $\rho$ , and ■, refractive indices,  $n_D$ , against temperature and fitted curves for pure [empy][EtSO<sub>4</sub>].**Figure 2.** Fractional deviations,  $\Delta\eta = \eta_{\text{exptl}} - \eta_{\text{calcd}}$ , of the experimental viscosities,  $\eta_{\text{exptl}}$ , of pure [empy][EtSO<sub>4</sub>] from values,  $\eta_{\text{calcd}}$ , obtained with the VFT equation (eq 4). ●, this work, with error bars representing the uncertainty; □, ref 2.

uncertainty of 0.01 s. To verify the calibration, viscosities of pure liquids were compared with bibliographic data (Table 1).

Densities were measured using an Anton Paar DSA-5000 digital vibrating tube densimeter. The repeatability and the uncertainty in experimental measurements have been found to be lower than ( $\pm 2\cdot 10^{-6}$  and  $\pm 1\cdot 10^{-5}$ )  $\text{g}\cdot\text{cm}^{-3}$ . The DSA 5000 automatically corrects the influence of viscosity on the measured density.

To measure refractive indices, an automatic refractometer Abbemat-HP Dr. Kernchen with an uncertainty in the experimental measurements of  $\pm 4\cdot 10^{-5}$  was used.

## Results and Discussion

**Pure Components.** The physical properties (density, viscosity, and refractive index) of [empy][EtSO<sub>4</sub>] were measured experimentally from (298.15 to 343.15) K. The values are summarized in Table 2.

The following equations were used to fit the density,  $\rho$ , and the refractive index,  $n_D$ , experimental values with the temperature.

$$\rho = a + b\cdot(T/\text{K}) + c\cdot(T/\text{K})^2 \quad (1)$$

$$n_D = d + e\cdot(T/\text{K}) \quad (2)$$

where  $T$  is the absolute temperature and  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are adjustable parameters.

**Table 5. Densities,  $\rho$ , Dynamic Viscosities,  $\eta$ , Refractive Indices,  $n_D$ , Excess Molar Volumes,  $V^E$ , Viscosity Deviations,  $\Delta\eta$ , and Deviations in the Refractive Index,  $\Delta n_D$ , of the Binary Mixture Ethanol (1) + [empy][EtSO<sub>4</sub>] (2) at Several Temperatures**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n_D$	$10^3\eta$ Pa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta n_D$	$10^3\Delta\eta$ Pa·s
$T = 298.15$ K						
0.0000	1.22226	1.50666	161.4	0.000	0.0000	0.000
0.0609	1.21493	1.50392	116.7	-0.117	0.0062	-34.960
0.1108	1.20833	1.50181	96.9	-0.200	0.0114	-46.709
0.2066	1.19393	1.49730	68.0	-0.336	0.0209	-60.293
0.3083	1.17571	1.49126	45.35	-0.460	0.0297	-66.613
0.4004	1.15573	1.48469	31.11	-0.540	0.0367	-66.089
0.4998	1.12953	1.47600	20.04	-0.620	0.0425	-61.232
0.6034	1.09496	1.46448	12.170	-0.674	0.0462	-52.490
0.7034	1.05168	1.45003	7.452	-0.709	0.0464	-41.177
0.8452	0.96167	1.41977	3.322	-0.596	0.0369	-22.576
0.9389	0.87077	1.38864	1.812	-0.405	0.0195	-9.065
1.0000	0.78546	1.36023	1.082	0.000	0.0000	0.000
$T = 313.15$ K						
0.0000	1.21254		77.1	0.000		0.000
0.0609	1.20503		55.2	-0.111		-17.208
0.1108	1.19838		48.57	-0.209		-20.082
0.2066	1.18386		36.25	-0.369		-25.091
0.3083	1.16553		25.91	-0.521		-27.676
0.4004	1.14551		18.88	-0.634		-27.680
0.4998	1.11907		12.922	-0.728		-26.057
0.6034	1.08430		8.317	-0.803		-22.760
0.7034	1.04072		5.332	-0.850		-18.117
0.8452	0.95009		2.502	-0.732		-10.131
0.9389	0.85852		1.388	-0.507		-4.099
1.0000	0.77200		0.827	0.000		0.000
$T = 328.15$ K						
0.0000	1.20286		42.32	0.000		0.000
0.0609	1.19520		31.20	-0.114		-8.579
0.1108	1.18852		28.12	-0.228		-9.581
0.2066	1.17391		21.86	-0.416		-11.853
0.3083	1.15546		16.41	-0.597		-13.059
0.4004	1.13536		12.518	-0.740		-13.114
0.4998	1.10874		8.971	-0.856		-12.518
0.6034	1.07373		6.023	-0.950		-11.148
0.7034	1.02983		3.990	-1.006		-9.013
0.8452	0.93848		1.943	-0.875		-5.150
0.9389	0.84610		1.086	-0.603		-2.102
1.0000	0.75855		0.641	0.000		0.000

The characteristic parameters  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  are given in Table 3 together with the root-mean-square deviations, rmsd.

$$\text{rmsd} = \left\{ \sum_i^{n_{\text{dat}}} (z - z_{\text{calcd}})^2 / n \right\}^{1/2} \quad (3)$$

where  $z$  and  $z_{\text{calcd}}$  are the values of the experimental and calculated property and  $n$  is the number of experimental data points.

The change of the molar volume with temperature can be expressed through the coefficient of thermal expansion,  $\alpha$ . With the experimental data of densities at the temperature range studied,  $\alpha$  can be calculated.

Figure 1 shows the density and the refractive index plotted against temperature. Over the temperature range studied, the refractive index decreases linearly with temperature. Differentiation of the equation that relates density with temperature gives a value of  $\alpha = 5.06 \cdot 10^{-4} \text{ K}^{-1}$  at  $T = 298.15$  K.

The viscosity values were fitted using the Vogel–Fulcher–Tamman (VFT) equation. According to Seddon et al.,<sup>11</sup> the Arrhenius law can generally be applied when the cation presents only a limited symmetry. If it is not the case, and especially in the presence of symmetrical cations, the Vogel–Fulcher–Tamman (VFT) equation is recommended.<sup>11–13</sup>

$$\eta = A \cdot T^{0.5} \exp\left(\frac{k}{T - T_0}\right) \quad (4)$$

where  $A$ ,  $k$ , and  $T_0$  are adjustable parameters. Table 4 lists the parameters for this equation together with the root-mean-square deviation (rmsd, eq 3).

Figure 2 shows fractional deviations,  $\Delta\eta = \eta_{\text{exptl}} - \eta_{\text{calcd}}$ , of the experimental viscosities,  $\eta_{\text{exptl}}$ , of pure [empy][EtSO<sub>4</sub>] from values,  $\eta_{\text{calcd}}$ , obtained with the VFT equation (eq 4) together with error bars representing the uncertainty. In this figure is also included a literature comparison.<sup>2</sup> The correlated values are in good agreement with the experimental data as shown in Table 4.

**Binary Systems.** Densities, dynamic viscosities, excess molar volumes, and viscosity deviations for the binary mixtures ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2) at temperatures of (298.15, 313.15, and 328.15) K and refractive indices and deviations in the refractive index at 298.15 K and atmospheric pressure are listed in Tables 5 and 6.

The excess molar volumes, viscosity, and refractive index deviations were calculated from experimental values as follows

**Table 6. Densities,  $\rho$ , Dynamic Viscosities,  $\eta$ , Refractive Indices,  $n_D$ , Excess Molar Volumes,  $V^E$ , Viscosity Deviations,  $\Delta\eta$ , and Deviations in the Refractive Index,  $\Delta n_D$ , of the Binary Mixture Water (1) + [empy][EtSO<sub>4</sub>] (2) at Several Temperatures**

$x_1$	$\rho$ g·cm <sup>-3</sup>	$n_D$	$10^3\eta$ Pa·s	$V^E$ cm <sup>3</sup> ·mol <sup>-1</sup>	$\Delta n_D$	$10^3\Delta\eta$ Pa·s
$T = 298.15$ K						
0.0000	1.22226	1.50666	161.4	0.000	0.0000	0.000
0.0526	1.22169	1.50583	127.6	-0.085	0.0083	-25.355
0.1412	1.22012	1.50427	102.1	-0.161	0.0222	-36.666
0.2445	1.21780	1.50193	77.9	-0.240	0.0379	-44.301
0.3233	1.21558	1.49986	62.3	-0.296	0.0495	-47.241
0.4174	1.21221	1.49685	46.87	-0.360	0.0629	-47.528
0.4972	1.20839	1.49329	36.11	-0.402	0.0732	-45.472
0.5880	1.20253	1.48806	26.83	-0.446	0.0838	-40.184
0.6975	1.19135	1.47838	17.72	-0.465	0.0932	-31.728
0.7928	1.17405	1.46398	11.177	-0.436	0.0954	-22.965
0.9005	1.12944	1.42959	4.927	-0.250	0.0798	-11.934
0.9484	1.0862	1.39796	2.717	-0.095	0.0565	-6.451
1.0000	0.9972	1.33251	0.89	0.000	0.0000	0.000
$T = 313.15$ K						
0.0000	1.21254		77.1	0.000		0.000
0.0526	1.21182		60.5	-0.058		-12.542
0.1412	1.21022		50.28	-0.126		-16.019
0.2445	1.20783		39.91	-0.192		-18.501
0.3233	1.20562		32.92	-0.246		-19.468
0.4174	1.20221		24.86	-0.302		-20.330
0.4972	1.19831		20.36	-0.335		-18.730
0.5880	1.19232		15.519	-0.367		-16.628
0.6975	1.18092		10.495	-0.371		-13.285
0.7928	1.16341		6.778	-0.334		-9.713
0.9005	1.11924		3.161	-0.164		-5.100
0.9484	1.0775		1.818	-0.044		-2.778
1.0000	0.9922		0.653	0.000		0.000
$T = 328.15$ K						
0.0000	1.20286		42.32	0.000		0.000
0.0526	1.20202		34.93	-0.036		-5.190
0.1412	1.20035		29.83	-0.092		-6.587
0.2445	1.19802		23.49	-0.164		-8.604
0.3233	1.19572		19.76	-0.206		-9.043
0.4174	1.19223		15.511	-0.253		-9.357
0.4972	1.18824		12.779	-0.277		-8.749
0.5880	1.18214		9.894	-0.301		-7.837
0.6975	1.17042		6.847	-0.288		-6.307
0.7928	1.15261		4.508	-0.241		-4.659
0.9005	1.10866		2.197	-0.087		-2.468
0.9484	1.0680		1.315	0.004		-1.346
1.0000	0.9857		0.504	0.000		0.000

$$V^E = \sum_{i=1}^N x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (5)$$

$$\Delta\eta = \eta - \sum_i x_i \eta_i \quad (6)$$

$$\Delta n_D = n_D - \sum_i x_i n_{D,i} \quad (7)$$

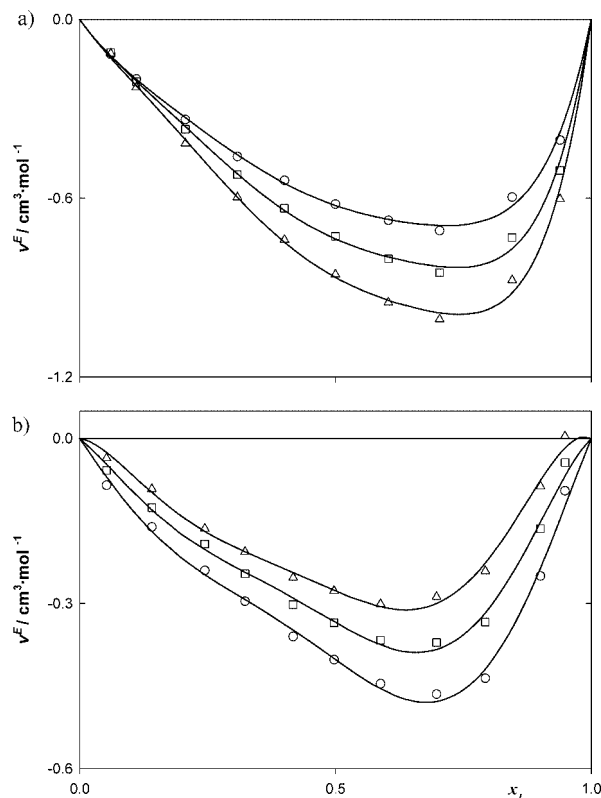
where  $\rho$  and  $\rho_i$  are the density of the mixture and the density of the pure components, respectively;  $x_i$  represents the mole fraction of the  $i$  component;  $\eta$  and  $\eta_i$  are the dynamic viscosity of the mixture and of the pure components, respectively; and  $n_D$  and  $n_{D,i}$  are the refractive index of the mixture and the refractive index of the pure components, respectively.

The binary deviations at several temperatures were fitted to a Redlich–Kister<sup>14</sup> type equation

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^M B_p (x_i - x_j)^p \quad (8)$$

where  $\Delta Q_{ij}$  is the excess property;  $x$  is the mole fraction;  $B_p$  is the fitting parameter; and  $M$  is the degree of the polynomial expansion, which was optimized using the F-test.<sup>15</sup> The fitting parameters are given in Table 7 together with the root-mean-square deviations (rmsd, eq 3).

Figures 3 and 4 show the fitted curves, as well as excess molar volume, and viscosity deviation values for binary mixtures: ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2) at  $T = (298.15, 313.15, \text{ and } 328.15)$  K. In Figure 3, it can be observed that the excess molar volumes present a minimum at  $x_1 \approx 0.7$  for the two systems. The minimum is more negative when temperature increases for the binary system containing ethanol and less negative when the temperature increases for the binary system containing water. The behavior of the excess molar volumes of the binary system water (1) + [empy][EtSO<sub>4</sub>] (2) can be explained because hydrogen bonding is certainly more temperature-dependent (becoming negligible at high temperatures) than Coulombic interactions. This result agrees with



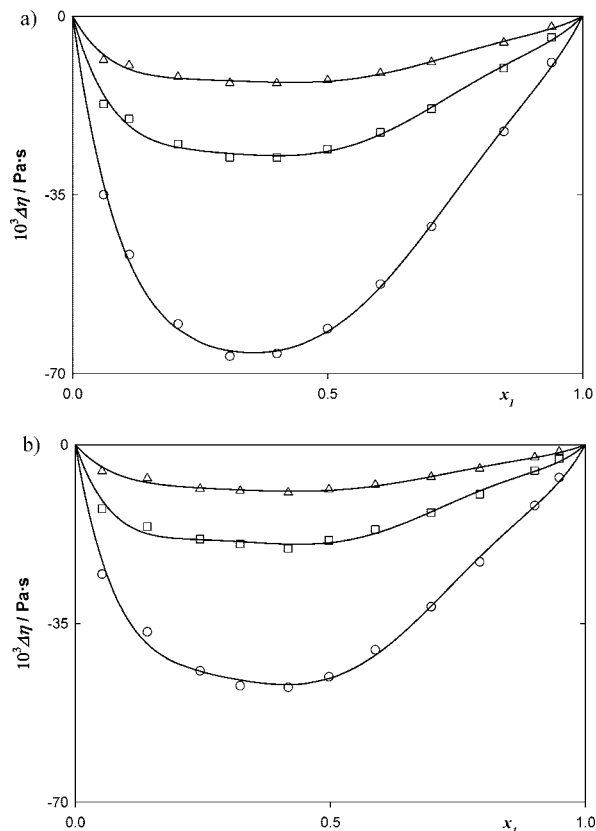
**Figure 3.** Excess molar volumes,  $V^E$ , plotted against mole fraction at  $\circ$ ,  $T = 298.15$  K;  $\square$ ,  $T = 313.15$  K; and  $\triangle$ ,  $T = 328.15$  K for the binary mixtures: (a) ethanol (1) + [empy][EtSO<sub>4</sub>] (2), (b) water (1) + [empy][EtSO<sub>4</sub>] (2), and —, fitted curves, using the Redlich–Kister parameters.

the work of Rebelo et al.<sup>16</sup> The minimum can be due to hydrogen bonds between water and ionic liquid. In Figure 4, for viscosity deviations, the sign is negative for the two binary systems, and the minima lie at a mole fraction of approximately 0.35 for ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and at 0.4 for water (1) + [empy][EtSO<sub>4</sub>] (2). The viscosity deviations decrease as the temperature increases, and this behavior is similar for both systems.

**Table 7.** Fitting Parameters and Root Mean Square Deviations (rmsd) for Ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and Water (1) + [empy][EtSO<sub>4</sub>] (2)

	$B_0$	$B_1$	$B_2$	$B_3$	$B_4$	rmsd
Ethanol (1) + [empy][EtSO <sub>4</sub> ] (2)						
$T = 298.15$ K						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-2.499	-1.190	-0.995	-1.736	-1.857	0.014
$10^3 \Delta\eta/\text{Pa} \cdot \text{s}$	-247.0	121.0	-12.67	140.7	-196.4	0.919
$\Delta n_D$	0.1696	0.0962	0.0674	0.0438		0.0001
$T = 313.15$ K						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-2.948	-1.510	-1.046	-2.555	-2.441	0.017
$10^3 \Delta\eta/\text{Pa} \cdot \text{s}$	-105.9	38.09	15.90	88.17	-136.8	0.788
$T = 328.15$ K						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-3.464	-1.886	-1.197	-3.158	-2.818	0.019
$10^3 \Delta\eta/\text{Pa} \cdot \text{s}$	-51.00	13.86	9.420	48.04	-72.47	0.441
Water (1) + [empy][EtSO <sub>4</sub> ] (2)						
$T = 298.15$ K						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-1.608	-1.313	-1.428	0.854	1.217	0.013
$10^3 \Delta\eta/\text{Pa} \cdot \text{s}$	-182.9	63.41	33.21	135.8	-227.3	1.140
$\Delta n_D$	0.2959	0.2177	0.1517	0.3631	0.3576	0.0011
$T = 313.15$ K						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-1.337	-1.060	-1.033	1.003	1.539	0.011
$10^3 \Delta\eta/\text{Pa} \cdot \text{s}$	-76.75	22.11	26.98	77.74	-137.0	0.748
$T = 328.15$ K						
$V^E/\text{cm}^3 \cdot \text{mol}^{-1}$	-1.108	-0.788	-0.765	1.082	1.990	0.010
$10^3 \Delta\eta/\text{Pa} \cdot \text{s}$	-35.73	11.124	8.644	24.93	-47.66	0.365





**Figure 4.** Viscosity deviations,  $\Delta\eta$ , plotted against mole fraction at  $\circ$ ,  $T = 298.15$  K;  $\square$ ,  $T = 313.15$  K; and  $\triangle$ ,  $T = 328.15$  K for the binary mixtures: (a) ethanol (1) + [empy][EtSO<sub>4</sub>] (2), (b) water (1) + [empy][EtSO<sub>4</sub>] (2), and —, fitted curves, using the Redlich–Kister parameters.

Comparing these results with those obtained for 1-ethyl-3-methylimidazolium ethylsulfate (EMISE),<sup>7</sup> which changes the cation with respect to the IL studied in this work, the behaviors of the excess molar volumes for both systems are very similar for the two ILs compared. In the behavior of the excess molar volumes, they present the minimum at the same mole fraction ( $x_1 \approx 0.7$ ), the  $V^E$  of aqueous solutions of [empy][EtSO<sub>4</sub>] being more negative and the  $V^E$  for systems containing ethanol being very similar. Differences are more remarkable for the viscosity deviations, where the location of the minimum can be considered similar ( $x_1 \approx 0.4$  for systems containing EMISE), but deviations from ideality for the systems with [empy][EtSO<sub>4</sub>] are higher than the deviations obtained for the same systems with EMISE.

## Conclusions

In this paper, we present the synthesis of an ionic liquid, [empy][EtSO<sub>4</sub>], together with its experimental values of density and dynamic viscosity from  $T = (298.15$  to  $343.15)$  K and refractive index at  $T = 298.15$  K. As usual, density, dynamic viscosity, and refractive index decrease as temperature increases.

Density and dynamic viscosity of the binary systems ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2) at  $T = (298.15, 313.15, \text{ and } 328.15)$  K and atmospheric pressure, over the whole composition range, have been determined.

The excess molar volumes and viscosity deviations for these binary systems were calculated from experimental data, and these data were fitted to the Redlich–Kister equation to test the quality of the experimental values. The obtained excess

molar volumes have different behavior depending on the binary system: for the binary system containing ethanol, the minimum is more negative when temperature increases, and for the binary system containing water, the trend is the opposite, according to the literature.<sup>16</sup> For the viscosity deviations, the deviation from ideality decreases as the temperature increases for both binary systems.

Refractive indices were measured at 298.15 K for the ethanol (1) + [empy][EtSO<sub>4</sub>] (2) and water (1) + [empy][EtSO<sub>4</sub>] (2). The results were used to calculate deviations in the refractive index. These deviations have positive values for both studied systems in the whole composition range.

## Literature Cited

- (1) Wassercheid, P.; Welton, T., Eds.; *Ionic liquids in synthesis*; Wiley-VCH: New York, 2003; p 364.
- (2) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559–568.
- (3) Zhao, D.; Fei, Z.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. Nitrile-functionalized pyridinium ionic liquids: synthesis, characterization, and their application in carbon-carbon coupling reactions. *J. Am. Chem. Soc.* **2004**, *126*, 15876–15882.
- (4) Papaiconomou, N.; Yakelis, N.; Salminen, J.; Prausnitz, J. M.; Bergman, R. Synthesis and properties of seven ionic liquids containing 1-methyl-3-octylimidazolium or 1-butyl-4-methylpyridinium cations. *J. Chem. Eng. Data* **2006**, *51*, 1389–1393.
- (5) Papaiconomou, S. J.; Lec, J. M.; Prausnitz, J. M. Physicochemical properties of hydrophobic ionic liquids containing 1-octylpyridinium, 1-octyl-2-methylpyridinium, or 1-octyl-4-methylpyridinium cations. *J. Chem. Eng. Data* **2007**, *52*, 833–840.
- (6) Gómez, E.; González, B.; Domínguez, A.; Tojo, E.; Tojo, J. Dynamic viscosities of a series of 1-alkyl-3-methylimidazolium chloride ionic liquids and their binary mixtures with water at several temperatures. *J. Chem. Eng. Data* **2006**, *51*, 696–701.
- (7) Gómez, E.; González, B.; Calvar, N.; Tojo, E.; Domínguez, A. Physical properties of pure 1-ethyl-3-methylimidazolium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096–2102.
- (8) Arce, A.; Rodríguez, O.; Soto, A. A comparative study on solvents for separation of Pert-amyl ethyl ether and ethanol mixtures. New experimental data for 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid. *Chem. Eng. Sci.* **2006**, *61*, 6929–6935.
- (9) Nikam, P.; Jadhav, M. C.; Hasan, M. Density and viscosity of mixtures of nitrobenzene with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, 2-methylpropan-1-ol, and 2-methylpropan-2-ol at 298.15 and 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 931–934.
- (10) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*; Wiley: New York, 1986.
- (11) Seddon, K. R.; Starck, A. S.; Torres, M. J. Viscosity and density of 1-alkyl-3-methylimidazolium ionic liquids III: Fundamentals, progress, challenges and opportunities. *ACS Symposium Series 901*, Washington DC, 2004.
- (12) Wilkes, J. S. Properties of ionic liquid solvents for catalysis. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17.
- (13) Okoturo, O. O.; Vandernoot, J. J. Temperature dependence of viscosity for room temperature ionic liquids. *J. Electroanal. Chem.* **2004**, *568*, 167–181.
- (14) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions, Algebraic representation of thermodynamic properties and the classification of solutions. *Ing. Eng. Chem.* **1948**, *40*, 345–348.
- (15) Bevington, P. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: N.Y., 1969.
- (16) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; Nunes da Ponte, M.; Szydłowski, J.; Cerdeiriña, C. A.; Troncoso, J.; Romani, L.; Esperança, J. M.; Guedes, S. S.; Sousa, M. C. A detailed thermodynamic analysis of [C<sub>4</sub>mim][BF<sub>4</sub>] + water as a case study to model ionic liquid aqueous solutions. *Green Chem.* **2004**, *6*, 369–381.

Received for review March 6, 2008. Accepted May 8, 2008. The authors are grateful to the Ministerio de Educación y Ciencia (project Acción Integrada: Iuso (E-32/06)-española (HP2005-0089)) for financial support.

JE800159W