Synthesis and Physical Properties of 1-Ethylpyridinium Ethylsulfate and its Binary Mixtures with Ethanol and 1-Propanol at Several Temperatures

Begoña González, Noelia Calvar, Elena Gómez, Irene Domínguez, and Ángeles Domínguez*

Departamento de Ingeniería Química de la Universidad de Vigo, 36310 Vigo, Spain

Ionic liquid 1-ethylpyridinium ethylsulfate, $EpyESO_4$, was synthesized, and its experimental densities, speeds of sound, viscosities, and refractive indices from (298.15 to 343.15) K are reported. Densities, speeds of sound, isentropic compressibility, and dynamic viscosities for $EpyESO_4$ + ethanol and + 1-propanol at temperatures T = (298.15, 313.15, and 328.15) K were determined over the whole composition range at 0.1 MPa. The excess molar volumes, isentropic compressibilities, and viscosity deviations for ethanol (1) + $EpyESO_4$ (2) and 1-propanol (1) + $EpyESO_4$ (2) binary systems at the above-mentioned temperatures were calculated and satisfactorily fitted to the Redlich−Kister equation. Refractive indices of the binary mixtures were measured at 298.15 K over the whole composition range. The results were used to calculate deviations in the refractive index.

Introduction

Ionic liquids (ILs) find a wide range of application as alternatives to the organic solvents for different processes, and they are being used as separation agents with very promising results, but experimental data of physical properties are still limited. Density and viscosity are, among other properties, important physical properties in the design of multiple processes. The most studied ILs are those containing ammonium and imidazolium cations. There are few investigations on ILs containing pyridinium cations.[1−6] In this work, we report three key thermophysical properties, density, refractive index, and viscosity, of the IL 1-ethylpyridinium ethylsulfate, $EpyESO_4$. This is a relatively new IL, and little information about its physical properties is available in literature.[2]

Thermodynamic properties of mixtures containing ILs are of great interest, so in this work the experimental density, speed of sound, refractive index, and dynamic viscosity of pure $EpyESO_4$ from T = (298.15 to 343.15) K are shown as an extension of our work concerning the dynamic viscosity of binary systems and the synthesis of ILs[6−8] to complete a database on physical properties of ILs. From experimental density data, the coefficient of thermal expansion, α, was calculated. Experimental density and dynamic viscosity data over the whole composition range for binary systems ethanol (1) + $EpyESO_4$ (2) and 1-propanol (1) + $EpyESO_4$ (2) have been determined at T = (298.15, 313.15, and 328.15) K and 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 the binary systems. The results were used to calculate deviations in the refractive index. No literature data for $EpyESO_4$ mixtures were found.

Experimental Section

Chemicals. Ethanol was supplied by Merck with purity higher than 99.8 %, and 1-propanol was supplied by Sigma-Aldrich with purity higher than 99.9 %. They were ultrasonically degassed and dried over molecular sieves type 4 Å supplied by Aldrich and kept under an inert argon atmosphere. Table 1 shows a comparison between experimental and literature data of pure components at 298.15 K.

Synthesis. We synthesized 1-ethylpyridinium ethylsulfate in our laboratory by following the standard synthesis for other

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

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

	ρ/g·cm^{-3}		n_D		$10^3\eta$/Pa·s	
component	exptl	lit	exptl	lit	exptl	lit
ethanol	0.7855	0.7854[a]	1.36023	1.35941[b]	1.082	1.082[a]
		0.78509[f]		1.35941[f]		1.0826[f]
1-propanol	0.7996	0.79960[b]	1.38310	1.38306[c]	2.017	1.951[c]
						2.0074[d]
		0.79975[f]		1.38370[f]		1.9430[f]
$EpyESO_4$	1.2520	n.a.[g]	1.50525	n.a.	126.3	137[E]

[a] From ref 10. [b] From ref 11. [c] From ref 12. [d] From ref 13. [e] From ref 2. [f] From ref 14. [g] n.a.: not available.

Table 2. Density, ρ, Refractive Index, n_D, Speed of Sound, u, and Dynamic Viscosity, η, of $EpyESO_4$at Several Temperatures

T/K	ρ/g·cm^{-3}	u/m·s^{-1}	n_D	$10^3\eta$/Pa·s
298.15	1.2520	1711	1.50525	126.3
303.15	1.2487	1699	1.50394	93.0
308.15	1.2454	1687	1.50258	72.1
313.15	1.2421	1676	1.50120	57.6
318.15	1.2388	1664	1.49976	46.4
323.15	1.2356	1653	1.49850	38.60
328.15	1.2323	1641	1.49720	32.53
333.15	1.2291	1630	1.49587	27.78
338.15	1.2259	1619	1.49454	23.90
343.15	1.2227	1608	1.49309	20.71

Table 3. Fitting Parameters of Equations *1* and *2* Together with the Deviations of the Fit (rmsd) for the Density and Refractive Index of $EpyESO_4$

physical properties	a	b	rmsd
ρ/g·cm^{-3}	1.446	$-6\cdot10^{-4}$	$4\cdot10^{-4}$
n_D	1.586	$-3\cdot10^{-4}$	$5\cdot10^{-5}$
u/m·s^{-1}	2389.5	−2.278	0.412

10.1021/je800981d CCC: $40.75
Published on Web 03/10/2009

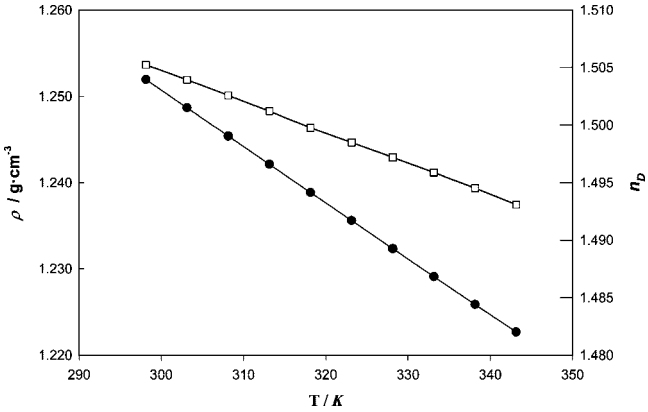

Figure 1. Plot of temperature against experimental values of: ●, densities (ρ); □, refractive indices (n_D); fitted curves for pure $EpyESO_4$.

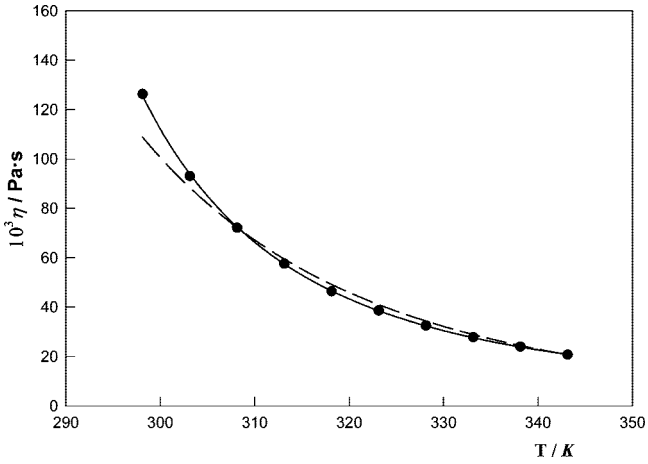

Figure 2. Plot of temperature against experimental values of: ●, viscosity (η); fitted curves: —, using the VFT parameters; ---, using the Arrhenius equation for pure $EpyESO_4$.

sulfate ILs, as published elsewhere.[8] The chemicals used for this synthesis were pyridine and diethylsulfate, both purchased from Sigma-Aldrich with a purity higher than 99 %. The obtained IL was dried by heating to (343.15 to 353.15) K and stirred under high vacuum ($2 \cdot 10^{-1}$ Pa) for 48 h. To ensure its purity, a NMR was performed: ^{1}H NMR (400 MHz, D_2O, δ): 8.87 (d, 2H, J = 5.6 Hz, oH), 8.54 (t, 1H, J = 7.8 Hz, pH), 8.08 (t, 2H, J = 7.1 Hz, mH), 4.66 (dd, 2H, J = 7.4 Hz, N−CH_2−CH_3), 4.07 (dd, 2H, J = 7.1 Hz, O−CH_2−CH_3), 1.64 (t, 3H, J = 7.4 Hz, N−CH_2−CH_3), 1.27 (t, 3H, J = 7.1 Hz, O−CH_2−CH_3). Its purity is higher than 99 % mass fraction.

The IL 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 its use.

Table 1 shows a comparison between experimental and literature data of the pure components at T = 298.15 K. Compared with literature, the viscosity values reported by Crosthwaite et al.[2] for pure $EpyESO_4$ are higher than our values. The difference can be due to the water content of IL, nonvolatile impurities in their samples or our samples, or different experimental techniques for measuring the viscosity.

Apparatus and Procedure. Samples were prepared by syringing known masses of the pure liquids into stoppered bottles in an inert-atmosphere glovebox. For mass measurements, a Mettler AX-205 delta range balance with a precision of ± 10^{-5} g was used. A glovebox was used because the IL is hygroscopic. 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.

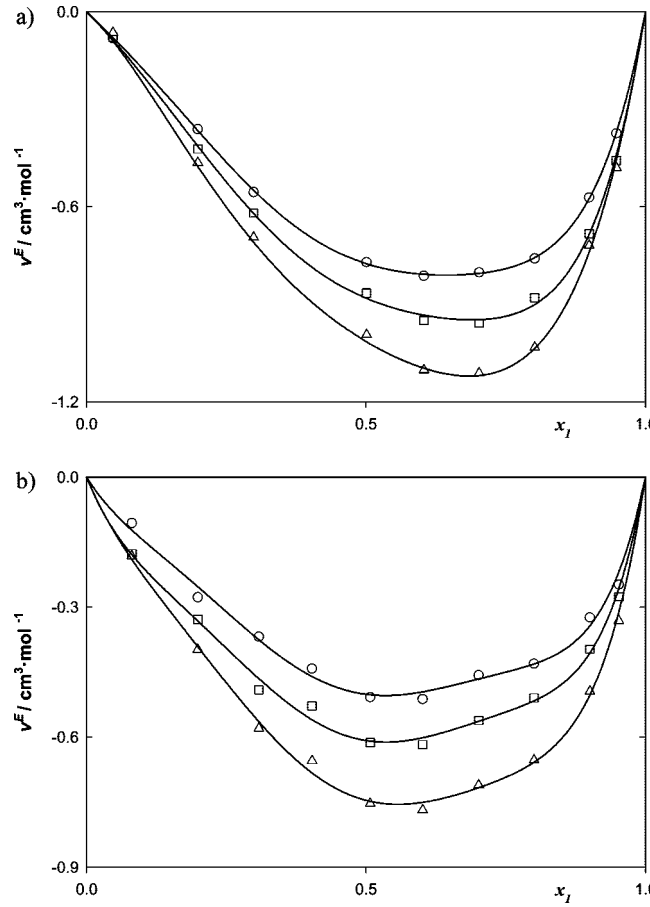

Figure 3. Excess molar volumes, V^E, plotted against mole fraction at: ○, T = 298.15 K; □, T = 313.15 K; and △, T = 328.15 K for the binary mixtures (a) ethanol (1) + $EpyESO_4$ (2) and (b) 1-propanol (1) + $EpyESO_4$ (2) and fitted curves using the Redlich−Kister parameters.

Table 4. Adjustable Parameters of the VFT Equation (A, k, and T_0) and Arrhenius Equation (n and E_a) Together with the Deviation of the Fit (rmsd) for the Viscosity of Pure $EpyESO_4$

	A / mPa·s·K	k / K	T_0 / K	rmsd
VFT equation	0.0317	468.7	211.9	0.010
	n	E_a		rmsd
Arrhenius equation	0.0003	−31303		0.100

Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with four Ubbelhode 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 was (± 0.001, ± 0.01, ± 0.03, and ± 0.2) mPa·s, respectively.) Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary was 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 uncertainty of 0.01 s. To verify the calibration, we compared viscosity of pure liquids with bibliographic data (Table 1).

Table 5. Densities, ρ, Dynamic Viscosities, η, Refractive Indices, n_D, Speeds of Sound, u, Isentropic Compressibilities, κ_S, Excess Molar Volumes, V^E, Viscosity Deviations, $\Delta\eta$, and Deviations in the Refractive Index, Δn_D, and Deviations in Isentropic Compressibility, $\Delta\kappa_S$, of the Binary Mixture Ethanol (1) + $EpyESO_4$ (2) at Several Temperatures

x_1	ρ / g·cm^{-3}	$10^3\eta$ / Pa·s	n_D	u / m·s^{-1}	κ_S / TPa^{-1}	V^E / cm^3·mol^{-1}	$10^3\Delta\eta$ / Pa·s	Δn_D	$\Delta\kappa_S$ / TPa^{-1}
				$T = 298.15$ K					
0.0000	1.2520	126.3	1.50252	1711	272.9	0.000	0.00	0.0000	0.0
0.0476	1.2453	103.3	1.50313	1700	277.7	−0.082	−17.04	0.0074	−28.2
0.1993	1.2208	58.4	1.49585	1661	297.0	−0.362	−42.98	0.0217	−114.6
0.2992	1.2012	40.3	1.48987	1630	313.5	−0.555	−48.51	0.0299	−167.6
0.5009	1.1472	17.27	1.47321	1546	364.9	−0.771	−46.30	0.0420	−256.6
0.6033	1.1092	10.79	1.46152	1491	405.4	−0.812	−39.96	0.0448	−287.3
0.7023	1.0620	6.63	1.44693	1428	462.0	−0.802	−31.73	0.0443	−299.6
0.8016	0.9999	3.947	1.42734	1349	549.1	−0.759	−21.98	0.0389	−281.6
0.8990	0.9155	2.244	1.40078	1258	689.7	−0.571	−11.48	0.0262	−208.9
0.9476	0.8601	1.641	1.38342	1206	798.9	−0.374	−6.00	0.0157	−133.5
1.0000	0.7855	1.082	1.36023	1146	968.9	0.000	0.00	0.0000	0.0
				$T = 313.15$ K					
0.0000	1.2421	57.6		1676	286.7	0.000	0.00		0.0
0.0476	1.2353	50.3		1665	292.0	−0.078	−4.64		−32.7
0.1993	1.2108	33.90		1625	312.7	−0.422	−12.39		−133.0
0.2992	1.1909	23.51		1593	330.8	−0.620	−17.12		−194.6
0.5009	1.1364	11.39		1508	386.8	−0.865	−17.78		−299.5
0.6033	1.0984	7.07		1453	431.4	−0.950	−16.28		−336.7
0.7023	1.0510	4.800		1388	493.8	−0.958	−12.93		−353.3
0.8016	0.9881	2.943		1308	591.6	−0.880	−9.15		−334.6
0.8990	0.9033	1.717		1214	751.5	−0.684	−4.84		−252.5
0.9476	0.8475	1.261		1160	877.5	−0.458	−2.54		−165.3
1.0000	0.7720	0.827		1093	1084.6	0.000	0.00		0.0
				$T = 328.15$ K					
0.0000	1.2323	38.60		1641	301.1	0.000	0.00		0.0
0.0476	1.2253	34.14		1631	306.7	−0.065	−2.66		−37.8
0.1993	1.2007	22.38		1591	329.1	−0.464	−8.65		−153.5
0.2992	1.1807	15.20		1558	349.0	−0.694	−12.04		−224.5
0.5009	1.1259	8.015		1472	410.0	−0.994	−11.57		−347.1
0.6033	1.0877	5.198		1388	477.1	−1.101	−10.50		−373.2
0.7023	1.0399	3.642		1350	527.9	−1.111	−8.30		−412.5
0.8016	0.9766	2.287		1267	637.6	−1.032	−5.89		−393.2
0.8990	0.8901	1.344		1170	821.0	−0.719	−3.13		−298.5
0.9476	0.8341	0.987		1113	967.4	−0.479	−1.64		−196.3
1.0000	0.7586	0.641		1043	1211.4	0.000	0.00		0.0

Densities and speeds of sound were measured using an Anton Paar DSA-48 digital vibrating-tube densimeter. The DSA-48 densimeter has no viscosity correction, so a calibration curve was performed to permit the measurement of densities of samples with high viscosity values. The uncertainty in experimental measurements has been found to be lower than $\pm 10^{-4}$ g·cm^{-3} for the density and ± 1 m·s^{-1} for the speed of sound. The apparatus was calibrated by air according to the manual instruction. The calibration was checked with pure liquids shown in Table 1.

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

Results and Discussion

Pure Components. The physical properties (density, viscosity, and refractive index) of $EpyESO_4$ were measured experimentally from (298.15 to 343.15) K. The values are summarized in Table 2.

The following equation was used to fit the density, ρ, speed of sound, u, and refractive index, n_D, experimental values with the temperature

$$z = a + b(T/\mathrm{K}) \tag{1}$$

where z is ρ, n_D, or u, T is the absolute temperature, and a and b are adjustable parameters. The characteristic parameters, a and b, are given in Table 3 together with the root-mean-square deviations (rmsd) calculated from eq 2. These properties (density, refractive index, and speed of sound) decrease as the temperature increases. Figure 1 shows the density and the refractive index plotted against temperature. Over the temperature range studied, the density and the refractive index decrease linearly with temperature

$$\mathrm{rmsd} = \left\{ \sum_i^{n_{dat}} (z - z_{calcd})^2 / n_{dat} \right\}^{1/2} \tag{2}$$

where z and z_{calcd} are the values of the experimental and calculated property and n_{dat} is the number of experimental data points.

The change in the molar volume with temperature can be expressed through the coefficient of thermal expansion, α. With the experimental data of densities, ρ, over the temperature range studied, α ($\alpha = (-1/\rho)(\partial\rho/\partial T)_P$ can be calculated. The α value is obtained from the slope of the representation of ln ρ against temperature. A value $\alpha = 5.26 \cdot 10^{-4}$ K^{-1} was obtained.

The viscosity values, η, were fitted using Arrehenius-like law and the Vogel−Fulcher−Tamman (VFT) equations. The most

Table 6. Densities, ρ, Dynamic Viscosities, η, Refractive Indices, n_D, Speeds of Sound, u, Isentropic Compressibilities, κ_S, Excess Molar Volumes, V^E, Viscosity Deviations, $\Delta\eta$, and Deviations in the Refractive Index, Δn_D, and Deviations in Isentropic Compressibility, $\Delta\kappa_S$, of the Binary Mixture Propanol (1) + EpyESO$_4$ (2) at Several Temperatures

x_1	ρ / g·cm^{-3}	$10^3\eta$ / Pa·s	n_D	u / m·s^{-1}	κ_S / TPa^{-1}	V^E / cm^3·mol^{-1}	$10^3\Delta\eta$ / Pa·s	Δn_D	$\Delta\kappa_S$ / TPa^{-1}
				$T = 298.15$ K					
0.0000	1.2520	126.3	1.50525	1711	272.9	0.000	0.00	0.0000	0.0
0.0814	1.2372	95.2	1.50137	1689	283.3	−0.124	−20.99	0.0061	−37.2
0.1994	1.2127	62.7	1.49499	1649	303.2	−0.276	−38.82	0.0141	−86.4
0.3084	1.1861	43.6	1.48804	1608	326.0	−0.399	−44.40	0.0205	−127.5
0.4035	1.1590	30.03	1.48081	1565	352.1	−0.491	−46.12	0.0248	−157.1
0.5077	1.1238	20.12	1.47142	1516	387.2	−0.548	−43.08	0.0282	−183.0
0.6013	1.0858	13.68	1.46126	1466	428.6	−0.545	−37.89	0.0295	−196.4
0.7016	1.0367	8.840	1.44802	1409	486.1	−0.513	−30.27	0.0285	−197.6
0.8004	0.9769	5.597	1.43181	1347	564.3	−0.447	−21.22	0.0243	−177.2
0.9002	0.9006	3.483	1.41100	1279	679.0	−0.332	−10.94	0.0157	−121.0
0.9521	0.8524	2.676	1.39773	1244	758.6	−0.252	−5.29	0.0088	−71.8
1.0000	0.7996	2.017	1.38310	1207	858.4	0.000	0.00	0.0000	0.0
				$T = 313.15$ K					
0.0000	1.2421	57.6		1676	286.7	0.000	0.00		0.0
0.0814	1.2274	48.0		1654	297.9	−0.161	−5.06		−42.9
0.1994	1.2027	34.23		1613	319.6	−0.327	−12.19		−99.7
0.3084	1.1761	25.21		1572	344.2	−0.490	−15.08		−147.7
0.4035	1.1485	18.31		1528	372.8	−0.552	−16.63		−182.4
0.5077	1.1130	12.91		1478	411.1	−0.611	−16.18		−213.4
0.6013	1.0748	9.161		1427	457.2	−0.616	−14.67		−229.6
0.7016	1.0252	6.131		1367	521.7	−0.561	−12.07		−231.7
0.8004	0.9653	3.988		1304	609.4	−0.509	−8.66		−209.8
0.9002	0.8889	2.507		1234	739.1	−0.397	−4.53		−146.5
0.9521	0.8403	1.921		1195	833.2	−0.276	−2.20		−87.0
1.0000	0.7874	1.430		1155	952.0	0.000	0.00		0.0
				$T = 328.15$ K					
0.0000	1.2323	38.60		1641	301.1	0.000	0.00		0.0
0.0814	1.2176	32.49		1619	313.3	−0.192	−3.05		−49.4
0.1994	1.1927	23.31		1578	336.6	−0.381	−7.80		−115.2
0.3084	1.1659	17.27		1537	363.3	−0.565	−9.74		−171.0
0.4035	1.1383	12.21		1493	394.3	−0.666	−11.23		−211.9
0.5077	1.1026	8.898		1440	437.1	−0.743	−10.63		−247.8
0.6013	1.0642	6.523		1388	487.4	−0.760	−9.49		−268.3
0.7016	1.0143	4.494		1327	559.4	−0.704	−7.76		−272.0
0.8004	0.9541	2.977		1262	658.1	−0.649	−5.56		−248.1
0.9002	0.8771	1.874		1189	806.8	−0.492	−2.92		−174.8
0.9521	0.8281	1.411		1147	917.2	−0.330	−1.43		−103.6
1.0000	0.7748	1.041		1105	1057.0	0.000	0.00		0.0

commonly used equation to correlate the variation of viscosity with temperature is the Arrhenius-like law

$$\eta = \eta_\infty \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

Viscosity at infinite temperature, η_∞, and the activation energy, E_a, are characteristic parameters generally adjusted from experimental data. According to Seddon et al.,[14] 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, then the VFT equation is recommended.[15−17]

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

where A, k, and T_0 are adjustable parameters. Table 4 lists the parameters for this equation together with the rmsd (eq 2). As can be observed in this table, for the viscosity, the better fitting is given by VFT. As can be seen in Figure 2, the correlated values are in good agreement with the experimental data. This Figure shows the viscosity against the temperature and the fitting using both equations (eqs 3 and 4). It can be observed that the viscosity decreases as the temperature increases.

Binary Systems. Densities, ρ, dynamic viscosities, η, speeds of sounds, u, isentropic compressibility, κ_S, excess molar volumes, V^E, viscosity deviations, $\Delta\eta$ and deviations in isentropic compressibility, $\Delta\kappa_S$, of the binary mixtures ethanol (1) + EpyESO$_4$ (2) and 1-propanol (1) + EpyESO$_4$ (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.

From speed of sound experimental data, the volume-intensive κ_S and the mole-intensive $\kappa_{S,m}$ can be calculated.[18−20] This mole-intensive quantity $\kappa_{S,m}$ depends on the heat capacities (C_p) of the pure components. Because, to our knowledge, no heat capacity of EpyESO$_4$ has been previously published, we have determined the κ_S by means of the Laplace equation, $\kappa_S = \rho^{-1} \cdot u^{-2}$.

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

$$V^{E} = \sum_{i=1}^{N} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (4a)$$

$$\Delta\eta = \eta - \sum_{i}^{N} x_i \eta_i \quad (5)$$

$$\Delta n_D = n_D - \sum_{i}^{N} x_i n_{D,i} \quad (6)$$

$$\Delta\kappa_S = \kappa_S - \sum_{i}^{N} x_i \kappa_{S,i} \quad (7)$$

where ρ and ρ_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; η and η_i are the dynamic viscosity of the mixture and of the pure components, respectively; n_D and $n_{D,i}$ are the refractive index of the mixture and the refractive index of the pure components, respectively; and κ_S is the isentropic compressibility of the mixture and $\kappa_{S,i}$ is the isentropic compressibility of the pure components.

The binary deviations at several temperatures were fitted to a Redlich−Kister-type[21] equation

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

Table 7. Fitting Parameters and Root-Mean-Square Deviations (rmsd) for Ethanol (1) + $EpyESO_4$ (2) and 1-Propanol (1) + $EpyESO_4$ (2)

Ethanol (1) + $EpyESO_4$ (2)						
	B_0	B_1	B_2	B_3	B_4	rmsd
			T = 298.15 K			
V^E/cm^3·mol^{-1}	−3.099	−1.094	−0.543	−2.609	−1.710	0.004
10^3 $\Delta\eta$/Pa·s	−182.90	88.45	−63.79	58.02		0.397
$\Delta\kappa_S$/TPa^{-1}	−1014.6	−686.2	−686.3	−568.6		2.96
Δn_D	0.166	0.089	0.076			0.00041
			T = 313.15 K			
V^E/cm^3·mol^{-1}	−3.525	−1.450	−1.079	−3.021	−1.592	0.012
10^3 $\Delta\eta$/Pa·s	−716.2	26.04	4.04	1.25		0.361
$\Delta\kappa_S$/TPa^{-1}	−1181.7	−805.3	−861.7	−772.2		4.53
			T = 328.15 K			
V^E/cm^3·mol^{-1}	−4.058	−2.038	−1.860	−2.447	−0.099	0.015
10^3 $\Delta\eta$/Pa·s	−47.78	21.27	3.15	−12.31		0.236
$\Delta\kappa_S$/TPa^{-1}	−1345.3	−900.6	−1098.1	−10.33.5		5.86
1-Propanol (1) + $EpyESO_4$ (2)						
	B_0	B_1	B_2	B_3	B_4	rmsd
			T = 298.15 K			
V^E/cm^3·mol^{-1}	−2.192	−0.444	0.856	−1.468	−2.853	0.012
10^3 $\Delta\eta$/Pa·s	−173.08	81.16	−38.58	23.11		0.239
$\Delta\kappa_S$/TPa^{-1}	−720.57	−398.10	−312.40	−220.62		1.35
Δn_D	0.112	0.053	0.026			0.00025
			T = 313.15 K			
V^E/cm^3·mol^{-1}	−2.456	−0.283	0.580	−1.900	−3.028	0.010
10^3 $\Delta\eta$/Pa·s	−65.42	19.94	5.15	−9.86		0.194
$\Delta\kappa_S$/TPa^{-1}	−837.7	−470.6	−398.7	−307.1		1.88
			T = 328.15 K			
V^E/cm^3·mol^{-1}	−2.979	−0.688	0.582	−1.934	−3.528	0.008
10^3 $\Delta\eta$/Pa·s	−43.15	15.05	7.05	−12.54		0.166
$\Delta\kappa_S$/TPa^{-1}	−974.0	−562.0	−494.0	−386.6		2.18

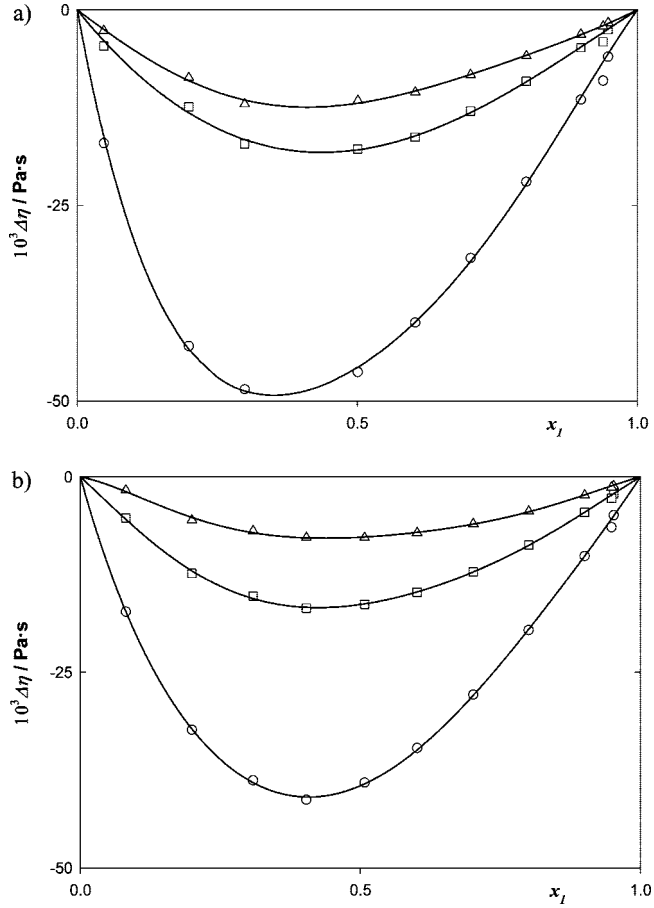

Figure 4. Viscosity deviations, $\Delta\eta$, plotted against mole fraction at ○, T = 298.15 K; □, T = 313.15 K; and △, T = 328.15 K for the binary mixtures (a) ethanol (1) + $EpyESO_4$ (2) and (b) 1-propanol (1) + $EpyESO_4$ (2) and fitted curves using the Redlich−Kister parameters.

where ΔQ_{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. The fitting parameters are given in Table 7 together with the rmsds (eq 2).

Figures 3 and 4 show the fitted curves as well as excess molar volume and viscosity deviations values for binary mixtures ethanol (1) + $EpyESO_4$ (2) and 1-propanol (1) + $EpyESO_4$ (2) at T = (298.15, 313.15, and 328.15) K. It can be observed in Figure 3 that the excess molar volumes present a minimum at a mole fraction of approximately $x_1 \approx 0.65$ for the system with ethanol and at $x_1 \approx 0.6$ for the system with propanol. The minimum is more negative when temperature increases for both binary systems. As can be observed, the excess molar volume is less negative when the aliphatic chain of alcohol increases. 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) + $EpyESO_4$ (2) and 0.4 for 1-propanol (1) + $EpyESO_4$ (2). The viscosity deviation decreases as the temperature increases, and as occurs in the excess molar volume, this excess is less negative when the aliphatic chain of alcohol increases; this behavior is similar for both systems.

Comparing these results with those obtained for 1-ethyl-3-methylimidazolium ethylsulfate (EMim ESO_4),[8] which changes the cation with respect to the IL studied in this work, and with those obtained for $EMpyESO_4$,[6] which changes the aliphatic chain of the cation, the behavior of the excess molar volumes for both binary systems are very similar for the three ILs compared. The excess molar volumes present the minimum at

approximately the same mole fraction ($x_1 \approx 0.7$); the V^E for systems containing ethanol is very similar. Differences are more remarkable for the viscosity deviations, where the location of the minimum can be considered to be similar for the three ILs, but deviations from ideality for the systems with $EMpyESO_4$[6] are higher than the deviations obtained for the other systems.

Conclusions

In this article, the synthesis of an IL, $EpyESO_4$, together with its experimental values of density, speed of sound, refractive index, and dynamic viscosity from $T = (298.15$ to $343.15)$ K are presented. As usual, density, dynamic viscosity, speed of sound, and refractive index decrease as temperature increases.

Density, speed of sound, and dynamic viscosity of the binary systems ethanol (1) + $EpyESO_4$ (2) and 1-propanol (1) + $EpyESO_4$ (2) at $T = (298.15$, 313.15, and 328.15) K and at 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. Both excess present a minimum over the whole composition range, and both are less negative when the aliphatic chain of the alcohol increases. The minimum of the excess molar volume is more negative when the temperature increases for both binary systems. 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) + $EpyESO_4$ (2) and 1-propanol (1) + $EpyESO_4$ (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) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 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.; Salminem, 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, Salminem, 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) González, B.; Calvar, N.; Gómez, E.; Macedo, E. A.; Domínguez, A. Synthesis and physical properties of 1-ethyl 3-methylpyridinium ethylsulfate and its binary mixtures with ethanol and water at several temperatures. *J. Chem. Eng. Data* **2008**, *53*, 1824–1828.

(7) 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.

(8) 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.

(9) Arce, A.; Rodríguez, O.; Soto, A. A comparative study on solvents for separation of *tert*-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.

(10) 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.

(11) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*; 4th ed.; Wiley: New York, 1986.

(12) Arce, A.; Rodil, E.; Soto, A. Physical and excess properties for binary mixtures of 1-methyl-3-octylimidazolium tetrafluoroborate, [Omim]-[BF4], ionic liquid with different alcohols. *J. Solution Chem.* **2006**, *35*, 63–78.

(13) Pal, A.; Sharma, S. Excess molar volumes and viscosities of 1-propanol + ethylene glycol + ethylene glycol monomethyl, + ethylene glycol dimethyl, + diethylene glycol dimethyl, + tri-ethylene glycol dimethyl, + diethylene glycol diethyl, and + diethylene glycol dibutyl ethers at 298.15 K. *J. Chem. Eng. Data* **1998**, *43*, 532–536.

(14) TRC Databases for Chemistry and Engineering, TRC Thermodynamic Tables; Texas Engineering Experimental Section, Texas A&M University System: College Station, TX, 1991−1998.

(15) Seddon, K. R.; Starck, A. S.; Torres, M. J. Viscosity and Density of 1-Alkyl-3-methylimidazolium. In *Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2004.

(16) Wilkes, J. S. Properties of ionic liquid solvents for catalysis. *J. Mol. Catal. A: Chem.* **2004**, *214*, 11–17.

(17) Okoturo, O. O.; Vandernoot, J. J. Temperature dependence of viscosity for room temperature ionic liquids. *J. Electroanal. Chem.* **2004**, *568*, 167–181.

(18) Douhéret, G.; Davis, M. I.; Reis, J. C. R.; Blandamer, M. J. Isentropic compressibilities: experimental origin and the quest for their rigorous estimation in thermodynamically ideal liquid mixtures. *Chem. Phys. Chem.* **2001**, *2*, 148–161.

(19) Douhéret, G.; Davis, M. I.; Reis, J. C. R.; Fjellanger, I. J.; Vaage, M. B.; Hoiland, H. Aggregative processes in aqueous solutions of isomeric 2-butoxyethanols at 298.15 K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6034–6042.

(20) Benson, G. C.; Kiyohara, O. Evaluation of excess isentropic compressibilities and isochoric heat capacities. *J. Chem. Thermodyn.* **1979**, *11*, 1061–1064.

(21) Redilch, O.; Kister, A. T. Thermodynamics of nonelectrolyte solutions, algebraic representation of thermodynamic properties and the classificacion of solutions. *Ing. Eng. Chem.* **1948**, *40*, 345–348.

Received for review December 19, 2008. Accepted February 16, 2009. We are grateful to the Ministerio de Educación y Ciencia of Spain (project CTQ2007-61272 and Ramón y Cajal Program RYC-2008-02388).

JE800981D