Viscosity and Electrical Conductivity of Binary Mixtures of C*n*MIM-BF$_4$ with Ethanol at 288 K, 298 K, 308 K, and 318 K

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In a recent paper we presented experimental measurements of the dynamic viscosity and specific electrical conductivity, for binary systems of 1-alkyl-3-methyl imidazolium tetrafluoroborate, [C*n*MIM][BF$_4$], with water. In this paper we complete those measurements with four systems of [C*n*MIM][BF$_4$] + ethanol, the alkyl chains of the ionic liquids (ILs) used being ethyl ([EMIM][BF$_4$]), butyl ([BMIM][BF$_4$]), hexyl ([HMIM][BF$_4$]), and octyl ([OMIM][BF$_4$]). As in aqueous systems, viscosity was measured at 288.15 K, 298.15 K, 308.15 K, and 318.15 K, while conductivity was measured at those four temperatures only for selected mixtures and at 298.15 K over the whole composition range. Note that [EMIM][BF$_4$] is only partially miscible with ethanol at the studied temperatures and atmospheric pressure (while it is completely miscible in water). We calculate viscosity deviations and molar conductivity from the original experimental data, which are compared with the scarce previously published data for similar mixtures and with the corresponding aqueous systems. Viscosity and electrical conductivity are related between them using Walden's rule, observing an increase of the resulting value with concentration. This behavior differs from that observed in the analogous aqueous systems.

Introduction

Ionic liquids (ILs) are molten salts made up usually of an anion and an organic large cation, which have melting temperatures below 373 K and usually below room temperature (in fact they are also known as room temperature ionic liquids, RTILs). Ethyl ammonium nitrate is the first discovered IL by Paul Walden in 1914, but the systematic study of ILs began with the present century.[1] The anion−cation electrostatic interactions are weak in the ILs due to the cation size, but if cation size is too large, the van der Waals forces between the alkyl chains of the IL molecules will increase the melting point.[1] The interest on ILs is due to their common and peculiar properties, such as good solubility of organic and inorganic compounds (including some metal salts), lack of vapor pressure, electrical conductivity, and high thermal and electrochemical stability. In addition, different combinations of the multiple anions and cations discovered to form ILs lead to billions of possible different compounds with very different physicochemical properties. So, in principle, we can design specific ionic liquids with the appropriate set of properties according to our purposes.[1]

One of the most interesting proposed industrial applications of ionic liquids is their use to improve the electrochemical and electrodeposition processes and also as electrolytes for batteries or solar cells.[2] These applications are based in their transport properties characteristics, mainly viscosity and electrical conductivity, so a proper knowledge and understanding is crucial to their development. It is necessary to experimentally measure those properties for pure ILs but also for mixtures with different solvents, including water and ethanol. For many applications it would be advantageous to use ILs mixed with other solvents to reduce its viscosity and increase its electrical conductivity, as published.[1−3]

In this work we present experimental measurements of dynamic viscosity and specific electrical conductivity on four binary mixtures of 1-alkyl-3-methyl imidazolium tetrafluoroborate [C*n*MIM][BF$_4$] with ethanol. Thus, the goal of this work is to study the alkyl chain length effect of the *n*-alkyl methyl imidazolium cation and to compare the two main transport magnitudes where movement of ions is generated by an electrical (conductivity) or mechanical (viscosity) field.

This work complements that published before with the same compounds mixed with water.[3] As in the previous paper, viscosity was measured at 288.15 K, 298.15 K, 308.15 K, and 318.15 K for the whole concentration range, while electrical conductivity was measured at the four temperatures only for one mixture, and it was measured for the whole concentration range at 298 K. The alkyl chains of the ILs used are ethyl [EMIM][BF$_4$], butyl [BMIM][BF$_4$], hexyl [HMIM][BF$_4$], and octyl [OMIM][BF$_4$]. It is important to remark that this family of ILs is one of the most popular for a number of electrochemical applications because of its relative high electrical conductivity and low viscosity compared with other IL families.[1,2] Note that [EMIM][BF$_4$] is only miscible with ethanol for an IL mole fraction higher than 0.53 at 298 K and atmospheric pressure, while it is completely miscible with water.[3] In contrast, at the same conditions [HMIM][BF$_4$] and [OMIM][BF$_4$] are completely miscible with ethanol but not with water. In fact, the only IL of the studied family which is miscible in the entire concentration range with water and ethanol is [BMIM][BF$_4$]. We have recently published densities for the ternary mixture

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10.1021/je100687x

Table 1. Water Mass Fraction, Molar Mass, Density, Viscosity, and Specific Conductivity at 273.15 K for [EMIM][BF$_4$], [BMIM][BF$_4$], [HMIM][BF$_4$], [OMIM][BF$_4$], and Ethanol[a]

	10^6 w	M / g·mol^{-1}	ρ / g·cm^3	η / mPa·s	η_{lit} / mPa·s	κ / mS·cm^{-1}	κ_{lit} / mS·cm^{-1}
[EMIM][BF$_4$]	220	197.98	1.2799[5]	36.93	37.19[11]	16.3	15.53[21] 15.46[22]
[BMIM][BF$_4$]	1040	226.03	1.2012[5]	99.20	100.66[12] 94.26[13] 153.78[14] 106.82[15]	3.52	3.53[21] 3.52[22] 5.86[15]
[HMIM][BF$_4$]	273	254.09	1.1454[5]	190.92	174.1[16] 210.4[17]	1.26	1.228[21] 1.229[22]
[OMIM][BF$_4$]	776	282.14	1.1042[5]	337.4	359.9[7] 341.0[18] 334.2[8] 325.0[19]	0.691	0.595[23] 0.583[7] 0.579[22]
ethanol	2000	46.07	0.7858[5]	1.091	1.083[20]	0.0005	0.000543[9]

[a] For viscosities and specific conductivities, literature values are also included.

Table 2

a. Dynamic Viscosity, η, Measured at Four Temperatures[a]

	η/mPa·s			
T/K	288.15	298.15	308.15	318.15
x_e		[EMIM] [BF$_4$] + Ethanol		
0.0000	55.50	36.90	26.00	19.17
0.0946	34.76	24.46	18.04	13.79
0.1928	25.25	18.33	13.88	10.84
0.2757	20.25	14.92	11.39	8.958
0.3116	18.17	13.47	10.38	8.238
0.3913	13.68	10.30	8.074	6.494
0.4553	12.47	8.445	6.668	5.408
1.0000	1.296	1.091	0.9153	0.7738
		[BMIM][BF$_4$] + Ethanol		
0.0000	173.5	99.20	61.30	40.40
0.0765	121.4	72.49	46.39	31.43
0.1990	69.06	44.05	29.81	21.16
0.2894	45.23	30.15	21.18	15.50
0.3918	28.39	19.70	14.45	11.01
0.4976	18.13	12.97	9.836	7.691
0.6001	12.35	9.038	7.026	5.567
0.7170	7.860	5.250	4.056	3.252
0.7998	5.676	4.286	3.363	2.723
0.9014	3.060	2.371	1.947	1.641

b. Dynamic Viscosity, η, Measured at Four Temperatures[a]

	η/mPa·s			
T/K	288.15	298.15	308.15	318.15
x_e		[HMIM][BF$_4$] + Ethanol		
0.0000	357.5	190.9	110.3	68.50
0.1000	207.2	119.2	74.2	48.17
0.1970	118.9	72.60	46.59	32.05
0.2980	69.02	43.77	29.55	21.19
0.3877	48.92	32.06	22.10	16.11
0.4921	27.71	18.86	13.73	10.30
0.6009	16.92	12.09	9.004	6.945
0.7000	9.866	7.513	5.487	4.498
0.8002	5.545	4.191	3.278	2.636
0.9020	2.893	2.284	1.867	1.506
		[OMIM][BF$_4$] + Ethanol		
0.0000	686.0	337.4	187.7	112.1
0.0891	428.3	224.8	132.1	81.45
0.1902	244.7	140.9	85.86	56.18
0.2927	141.0	83.3	53.62	36.49
0.3914	73.44	46.35	31.24	22.10
0.4911	45.24	29.85	20.79	15.44
0.5938	26.02	17.84	12.87	9.671
0.6979	14.53	10.39	7.756	6.015
0.7980	7.219	5.362	4.135	3.283
0.9002	3.499	2.764	2.206	1.802

[a] Concentration is expressed as the mole fraction of the ethanol, x_e.

[BMIM][BF$_4$] + water + ethanol at 298 K and seven pressures.[4] Also, this paper complements another one recently published by us, where we presented density and surface tension at 298 K for exactly the same systems measured here.[5]

To date, because of the lack of predicting models, the only way to know the transport properties of the IL mixtures is experimentally. However, the measurement of physical properties of ILs mixed with different substances was scarce until 2004,[6] but since then many papers have been published performing measurements on mixtures of ionic liquids with different kinds of solvents such as water, ethanol, aromatic compounds, or other ionic liquids, and the number of published papers is continuously growing.[1] Respecting the two magnitudes measured here and for ethanol mixtures with the same imidazolium IL family, we have found only two papers presenting dynamic viscosity[7,8] for the mixture [OMIM][BF$_4$] + ethanol and none for the other three systems studied here. In addition, we have not found any paper presenting experimental measurements of electric conductivity for any of the binary systems studied here.

Experimental Procedure

Viscosity was measured in an Anton Paar AMVn which is thermostatted with a Peltier cell with an uncertainty of ± 0.01 K. The repeatability in the measurement of the viscosity is about 0.3 %. The electrical conductivity was measured using a Crison GLP 31+ conductivimeter, which has an uncertainty of ± 10 nS·cm^{-1} or 1 % of the measured value. The samples were thermostatted in an external bath with an uncertainty of ± 0.1 K. Details of the electrical conductivity measurements are given in a previously published paper.[9] The ILs were purchased from Solvent Innovation (which has been recently adsorbed by Merck), and the purities are better than 99 % for all of them except for [EMIM][BF$_4$], which is better than 98 %. The ethanol used for the samples was from Panreac, and it has a purity better than 99.5 %. Because of the hygroscopic character of the ILs the chemicals were opened from its original tin and mixed with ethanol into a dry chamber, with a relative humidity grade lower than 10 %. This humidity grade, and the speed of the mixture process, ensures that our original ILs were not contaminated with water, as we recently studied quantitatively.[10] Mixtures were made by mass using a balance with a precision in the mass weight of ± 0.0001 g, which gives a mole fraction and concentration accuracy better than, respectively, $1 \cdot 10^{-4}$ mol·L^{-1} and $1 \cdot 10^{-3}$. The different mixtures were bottled and sealed before taking them out of the dry chamber. The water content

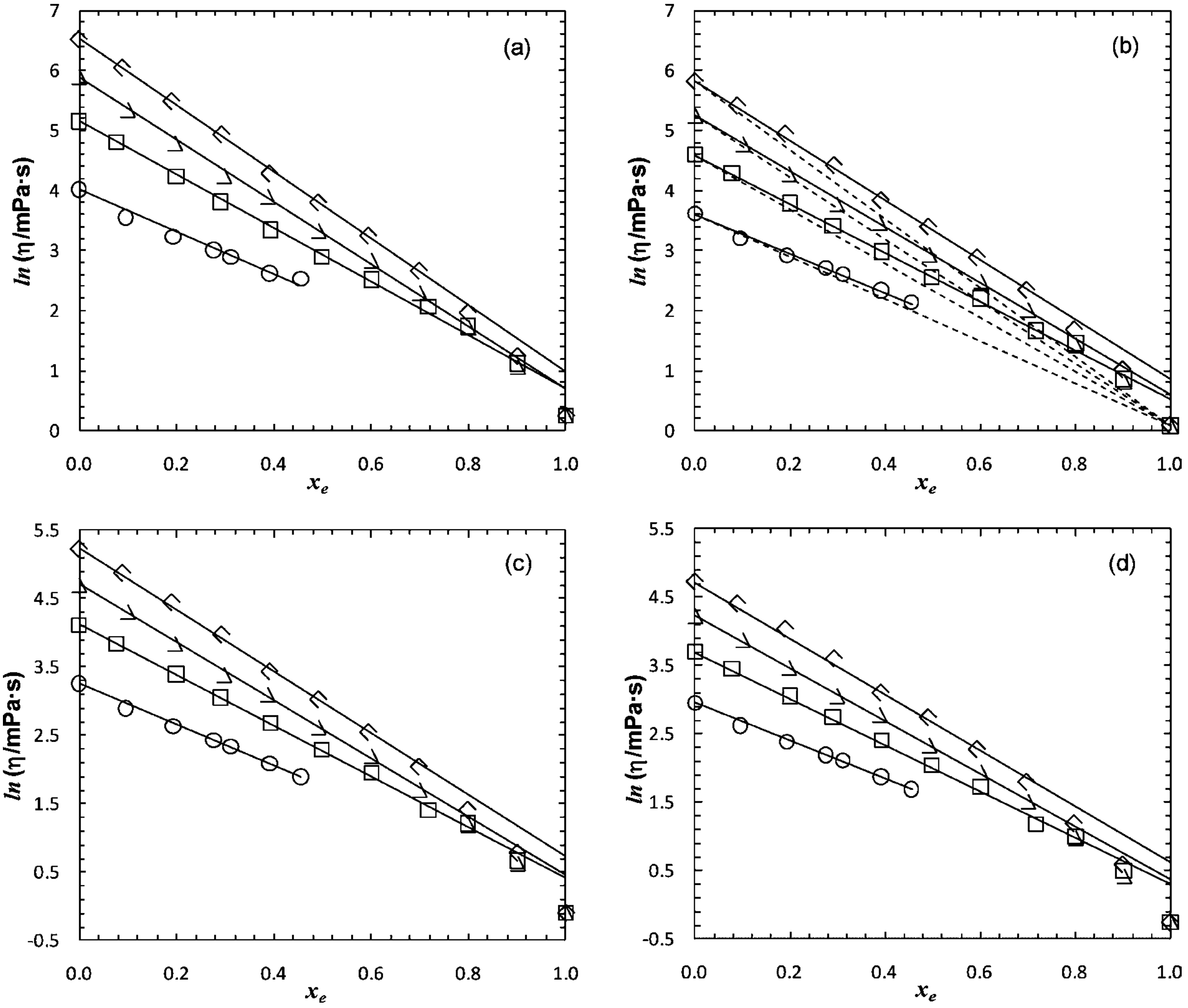

Figure 1. Natural logarithm of dynamic viscosity vs mole fraction of ethanol for the binary mixtures with [EMIM][BF$_4$] (dot symbols), [BMIM][BF$_4$] (square symbols), [HMIM][BF$_4$] (triangle symbols), and [OMIM][BF$_4$] (rhombus symbols) at (a) 288.15 K, (b) 298.15 K, (c) 308.15 K, and (d) 318.15 K. Solid lines are the best fit of eq 1 with the parameters given in Table 3 for ethanol mole fractions lower than 0.7. Dotted lines in b represent a perfect exponential behavior.

of the four ILs is lower than 1000 ppm, as certified by the dealer, and they were not further purified. The exact value of original water content is included in Table 1.

Results and Discussion

In Table 1 we show the molecular mass, M, density, ρ (previously published by us[5]), viscosity, η, and specific conductivity, κ, of the pure compounds used at 298.15 K. We compare the experimental η and κ data measured here with others published in literature.[11−23] Electrical conductivity data are very similar to that previously measured by Stoppa et al.[21,22] for [BMIM][BF$_4$] and [HMIM][BF$_4$], but for [EMIM][BF$_4$] and [OMIM][BF$_4$] the value measured here is about 5 % and 20 % higher, respectively, than that published before.[21−23] The reason could be the origin of the compounds used or hydrolysis of the BF$_4$ anion, as suggested in ref 22. For the available viscosity data in literature there is much dispersion, our values being within those given in Table 1.

In Table 2a and b we present dynamic viscosity data of all measured mixtures at the four temperatures used and atmospheric pressure. In Figure 1a−d we plot the natural logarithm of η versus the mole fraction of ethanol, x_e, for the data at 288.15 K, 298.15 K, 308.15 K, and 318.15 K, respectively. As observed, the obtained data fit to a straight line for all systems at the four temperatures for mixtures with $x_e < 0.7$. This means that in a broad region η versus x_e follows an exponential equation, as previously observed in similar systems with water.[3,7,9,24]

$$\ln \eta = \ln \eta_{IL} - \frac{x_e}{a} \tag{1}$$

where η_{IL} is the viscosity of pure IL. The best fitting a parameters for the four systems and four temperatures studied are given in Table 3, with the square of the regression factor, R^2, better than 0.99 for all fittings. In any case the data do not present a perfect exponential behavior for the whole concentration range because the corresponding fitting parameter a is not equal to $(\ln \eta_{IL} - \ln \eta_e)^{-1}$ (η_e being the viscosity of pure ethanol). This same behavior was observed in the [CnMIM][BF$_4$] + water systems, but in those cases the linearity between ln η and the mole fraction of water, x_w, extends up to $x_w < 0.9$.[3]

As usual, we have extracted the viscosity deviations upon mixing, $\Delta\eta$[3−9]

$$\Delta\eta = \eta - (x_{IL} \cdot \eta_{IL} + x_e \cdot \eta_e) \tag{2}$$

Table 3. Value of 1/*a* for the Best Fit of Natural Logarithm of Viscosity Versus the Mole Fraction of Ethanol Following Equation 1

	$[EMIM][BF_4]$ + Ethanol			
T/K	288.15	298.15	308.15	318.15
$1/a$	3.536	3.292	3.013	2.784
R^2	0.993	0.990	0.993	0.995
	$[BMIM][BF_4]$ + Ethanol			
T/K	288.15	298.15	308.15	318.15
$1/a$	4.441	4.073	3.700	3.386
R^2	0.998	0.999	0.999	0.997
	$[HMIM][BF_4]$ + Ethanol			
T/K	288.15	298.15	308.15	318.15
$1/a$	5.168	4.656	4.240	3.844
R^2	0.998	0.999	0.999	0.999
	$[OMIM][BF_4]$ + Ethanol			
T/K	288.15	298.15	308.15	318.15
$1/a$	5.531	4.952	4.505	4.102
R^2	0.999	0.999	0.998	0.997

where x_{IL} is the mole fraction of the ionic liquid (so $x_{IL} = 1 - x_e$). The obtained curves for the four temperatures are plotted in Figure 2a−d for, respectively, the systems with $[EMIM][BF_4]$, $[BMIM][BF_4]$, $[HMIM][BF_4]$, and $[OMIM][BF_4]$. All $\Delta\eta$ curves for the four systems and four temperatures studied are similar, increasing its absolute value with the alkyl chain of the IL but decreasing with temperature. They have their minimum skewed to rich IL concentrations, about $x_e = 0.3$. When compared with the water systems with the same ILs,[3] we observe that the results are very similar, both in amplitude (less than a 10 % higher in absolute value here) and also in the position of the minimum. Viscosity deviations on the mixture have been fitted using a new model with only four free parameters introduced by us, which reads,[5,25]

$$\Delta\eta = K \cdot {x_{IL}}^{n} \cdot x_e + K' \cdot x_{IL} \cdot {x_e}^{n'} \tag{3}$$

where K, n, K', and n' are fitting parameters, where the exponents n and n' are positive. The resulting curves are included in Figure 2a−d, and the fitting values, with the standard deviation, s, are given in Table 4a. Also, we have fitted our experimental viscosity deviation data to the most common Redlich−Kister equation[26]

$$\Delta\eta = x_{IL} x_e \sum_{K=0}^{m} A_K (x_{IL} - x_e)^K \tag{4}$$

where A_K denotes the polynomial fitting coefficients. The degree (m) of the polynomial Redlich−Kister equation was optimized by applying the F-test, where five coefficients ($m = 4$) are necessary to obtain standard deviations, s, lower or similar to those given by fitting eq 3. The obtained polynomial coefficients are included in

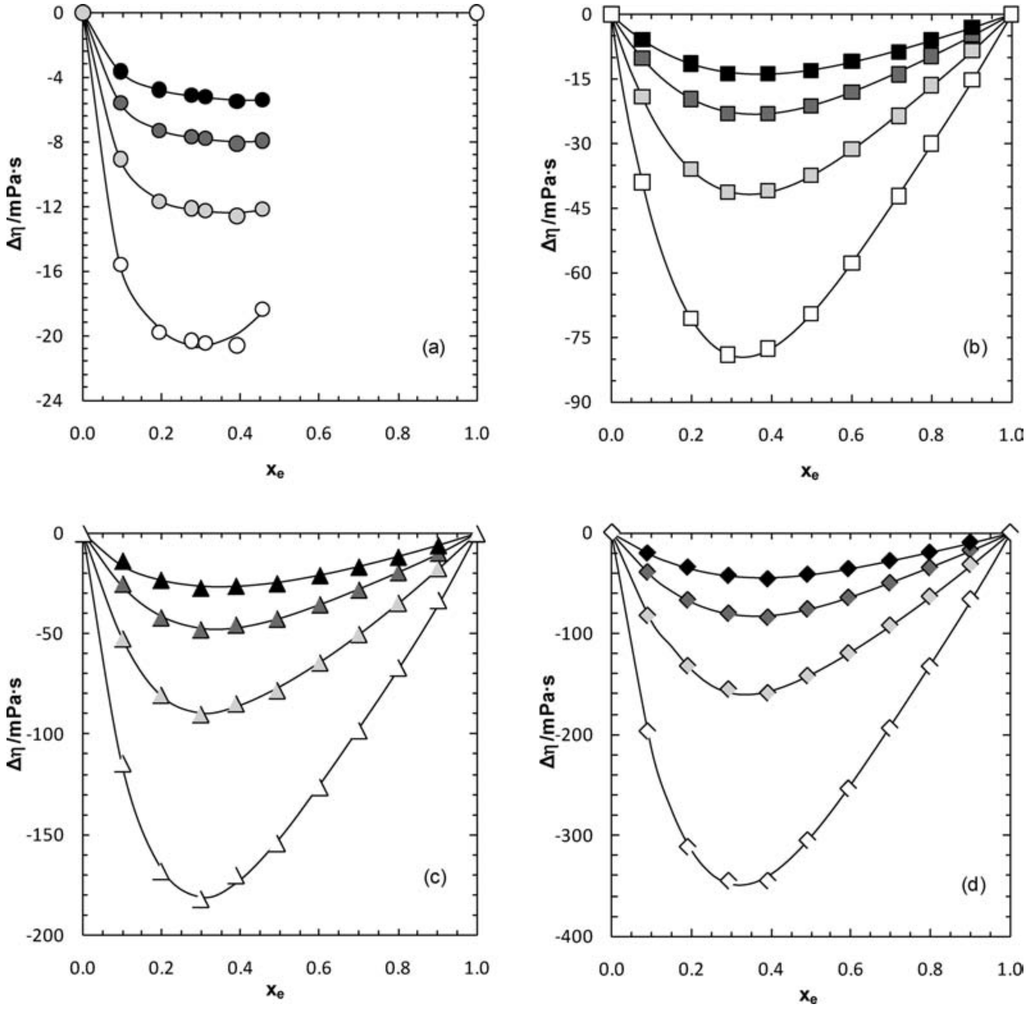

Figure 2. Dynamic viscosity deviations vs the ethanol mole fraction at 288.15 K (white symbols), 298.15 K (light gray symbols), 308.15 K (dark gray symbols), and 318.15 K (black symbols) for binary mixtures of (a) $[EMIM][BF_4]$, (b) $[BMIM][BF_4]$, (c) $[HMIM][BF_4]$, and (d) $[OMIM][BF_4]$. Solid lines are the best fit of novel eq 3 to the data with the parameters given in Table 4.

Table 4

a. Best Fitting Parameters of Equation 3 Used to Reproduce Viscosity Deviation Data

T/K	288.15	298.15	308.15	318.15
	[EMIM][BF$_4$] + Ethanol			
K	−64.33	−82.04	−52.98	−35.71
n	1.880	8.438	8.659	8.840
K'	−20.67	−41.32	−27.90	−19.56
n'	0.241	0.797	0.841	0.877
s	0.40	0.12	0.07	0.05
	[BMIM][BF$_4$] + Ethanol			
K	−343.2	−171.1	−90.85	−48.80
n	2.926	2.786	2.683	2.569
K'	−166.7	−92.23	−54.35	−33.74
n'	0.830	0.886	0.924	0.924
s	0.19	0.25	0.21	0.17
	[HMIM][BF$_4$] + Ethanol			
K	−931.0	−494.6	−285.1	−251.9
n	3.465	3.252	2.967	0.942
K'	−391.1	−205.6	−116.4	224.9
n'	0.837	1.004	1.274	1.452
s	1.98	1.09	0.85	0.31
	[OMIM][BF$_4$] + Ethanol			
K	−1527	−658.6	−516.1	−265.1
n	3.013	2.719	1.847	1.681
K'	−723.6	−339.5	−184.2	−98.87
n'	0.803	0.886	4.780	5.858
s	2.20	1.20	0.64	0.58

b. Best Fitting Parameters of Equation 4 Used to Reproduce Viscosity Deviation Data

T/K	288.15	298.15	308.15	318.15
	[EMIM][BF$_4$] + Ethanol			
A_0	−62.02	−45.68	−28.76	−19.85
A_1	−166.1	−46.30	−47.68	−28.54
A_2	356.5	104.9	164.5	100.1
A_3	−415.0	−172.3	−284.0	−172.8
A_4			105.4	62.13
s	0.17	0.05	0.01	0.02
	[BMIM][BF$_4$] + Ethanol			
A_0	−277.7	−149.1	−85.28	−51.71
A_1	−201.0	−97.83	−50.92	−27.64
A_2	−100.9	−47.47	−24.35	−14.06
A_3	−33.88	−10.93	−4.04	−3.06
A_4	−17.76	4.58	7.82	7.99
s	0.14	0.22	0.18	0.14
	[HMIM][BF$_4$] + Ethanol			
A_0	−604.6	−307.1	−166.6	−97.22
A_1	−464.7	−225.8	−117.7	−58.52
A_2	−396.8	−183.9	−108.3	−42.46
A_3	−165.4	−35.07	9.86	−7.53
A_4	75.83	79.12	96.87	23.65
s	1.32	0.84	0.59	0.27
	[OMIM][BF$_4$] + Ethanol			
A_0	−1208	−568.0	−300.1	−169.1
A_1	−904.5	−389.0	−192.1	−95.75
A_2	−487.3	−135.3	−56.28	−9.09
A_3	−178.7	−2.91	31.96	20.75
A_4	−95.60	−51.01	5.10	−16.59
s	1.99	1.18	0.61	0.55

Table 4b, while the curves are not drawn in Figure 2 because they are not distinguishable from those plotted from eq 3.

Table 5

a. Electrical Conductivity Measured Expressed in Ethanol Mole Fraction, x_e, and Molarity, c, at 298.15 K

x_e	c/mol·L^{-1}	κ/mS·cm^{-1}	x_e	c/mol·L^{-1}	κ/mS·cm^{-1}
		[EMIM][BF$_4$] + Ethanol			
0.0000	6.4598	16.30	0.3165	5.5377	29.82
0.0280	6.3935	17.18	0.3892	5.2475	32.28
0.0570	6.3226	18.43	0.4085	5.1878	32.78
0.0719	6.2855	19.11	0.4322	5.0560	32.60
0.1034	6.2041	20.61	0.4511	5.1633	34.70
0.1624	6.0418	22.87	0.4613	4.9668	35.61
0.2420	5.7980	26.47			
		[BMIM][BF$_4$] + Ethanol			
0.0000	5.3128	3.52	0.8908	1.5083	12.49
0.0368	5.2577	3.93	0.9034	1.3644	11.55
0.1136	5.1208	5.22	0.9134	1.2444	10.77
0.1492	5.0475	5.94	0.9217	1.1412	10.1
0.2992	4.6924	9.39	0.9287	1.0526	9.4
0.4162	4.3619	12.68	0.9347	0.9750	8.74
0.5137	4.0286	15.51	0.9399	0.9068	8.25
0.5866	3.7263	17.29	0.9493	0.7778	7.33
0.6426	3.4518	18.26	0.9564	0.6791	6.58
0.6863	3.2051	18.71	0.9617	0.6021	5.97
0.7204	2.9903	18.74	0.9668	0.5269	5.36
0.7498	2.7863	18.59	0.9755	0.3961	4.23
0.7947	2.4390	17.45	0.9897	0.1721	2.21
0.8394	2.0413	15.64	0.9916	0.1408	1.944
0.8763	1.6684	13.43	0.9934	0.1111	1.623
0.8835	1.5905	12.97	0.9972	0.0471	0.851

b. Electrical Conductivity Measured Expressed in Ethanol Mole Fraction, x_e, and Molarity, c, at 298.15 K

x_e	c/mol·L^{-1}	κ/mS·cm^{-1}	x_e	c/mol·L^{-1}	κ/mS·cm^{-1}
		[HMIM][BF$_4$] + Ethanol			
0.0000	4.5076	1.26	0.8755	1.5833	11.09
0.2439	4.1532	3.30	0.8857	1.4851	10.70
0.3981	3.8402	5.65	0.8946	1.3947	10.33
0.4566	3.6937	6.60	0.9042	1.2949	9.80
0.5070	3.5510	7.69	0.9133	1.1954	9.29
0.5491	3.4178	8.77	0.9214	1.1031	8.79
0.5861	3.2885	9.47	0.9267	1.0416	8.32
0.6189	3.1627	10.34	0.9347	0.9456	7.78
0.6450	3.0542	10.83	0.9437	0.8324	7.02
0.6708	2.9391	11.29	0.9526	0.7161	6.21
0.6938	2.8288	11.70	0.9593	0.6248	5.70
0.7145	2.7231	12.06	0.9686	0.4936	4.73
0.7330	2.6219	12.16	0.9758	0.3877	3.93
0.7495	2.5268	12.22	0.9803	0.3186	3.31
0.7648	2.4340	12.44	0.9858	0.2331	2.62
0.7909	2.2637	12.50	0.9892	0.1794	2.14
0.8217	2.0411	12.25	0.9934	0.1102	1.47
0.8454	1.8515	11.90	0.9960	0.0671	1.02
0.8637	1.6926	11.44	0.9979	0.0350	0.636
		[OMIM][BF$_4$] + Ethanol			
0.0000	3.9124	0.69	0.8138	1.9622	9.20
0.1236	3.7901	1.08	0.8320	1.8398	9.03
0.1830	3.7212	1.43	0.8472	1.7296	8.82
0.2395	3.6494	1.91	0.8663	1.5803	8.44
0.2898	3.5792	2.39	0.8814	1.4527	8.00
0.3359	3.5083	2.91	0.8938	1.3399	7.62
0.4147	3.3693	3.96	0.9087	1.1955	6.96
0.4783	3.2369	5.00	0.9197	1.0819	6.39
0.5316	3.1090	5.90	0.9307	0.9616	5.83
0.5759	2.9880	6.72	0.9409	0.8429	5.26
0.6135	2.8732	7.37	0.9502	0.7287	4.54
0.6455	2.7654	7.86	0.9586	0.6205	3.93
0.6799	2.6372	8.34	0.9692	0.4766	3.04
0.7089	2.5173	8.72	0.9771	0.3632	2.39
0.7381	2.3838	9.11	0.9851	0.2417	1.553
0.7667	2.2390	9.18	0.9915	0.1403	0.924
0.7922	2.0955	9.26	1.0000	0.0000	0.0003

We have look for published measurements similar to ours using the available database[27] and other sources. We have found only two papers reporting η for the system [OMIM][BF$_4$] + ethanol at 298 K[7,8] and no published results for the other binary systems measured. If we compare our present measurements with those previously reported in literature we observe that the agreement is good within experimental uncertainties. Even when Arce et al.[7] reports a 10 % higher value for the pure compound (see Table 1), the values for the different mixtures agree with

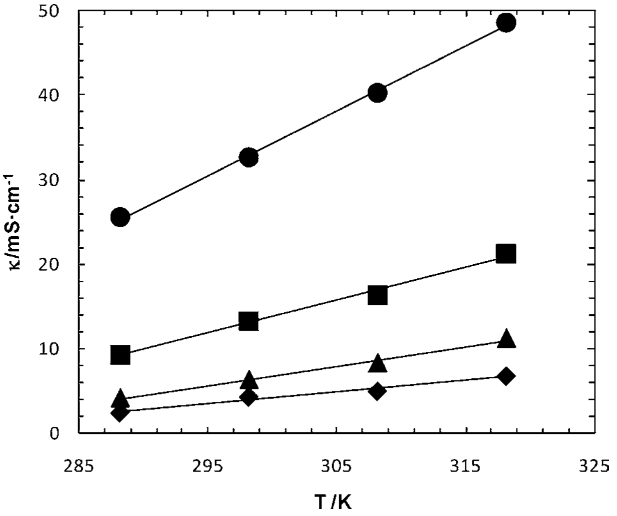

Figure 3. Temperature dependence of the selected binary mixtures with a mole fraction of ethanol (x_e) of about 0.435 and with the IL being: [EMIM][BF_4] (dot symbols), [BMIM][BF_4] (square symbols), [HMIM][BF_4] (triangle symbols), and [OMIM][BF_4] (rhombus symbols). Lines are the best fit of a straight line.

Table 6. Electrical Conductivity of Selected Mixtures at Four Temperatures

	κ/mS·cm^{-1}			
T/K	[EMIM][BF_4] $x_{IL} = 0.5678$	[BMIM][BF_4] $x_{IL} = 0.5631$	[HMIM][BF_4] $x_{IL} = 0.5675$	[OMIM][BF_4] $x_{IL} = 0.5659$
288.15	25.6	9.34	4.19	2.40
298.15	32.6	13.32	6.33	4.29
308.15	40.3	16.27	8.30	4.96
318.15	48.5	21.2	11.16	6.76

ours. In contrast, while our data for pure IL agree within 1 % with that published by Mokhtarani et al.,[8] our values are lower than theirs for the two most IL-rich mixtures, but sets of data agree again for more diluted mixtures.

In Table 5 we show the electrical conductivity data, κ, at 298.15 K for the [CnMIM][BF_4] + ethanol systems at all concentrations measured (expressed as ethanol mole fraction, x_e, and molarity, c). Part of these data was recently used by us to verify a pseudolattice theory of charge transport in ionic liquid + solvent mixtures, which gives a corresponding states law for the electric conductivity that fits the experimental data with high accuracy.[28]

In Figure 3 we plot the temperature dependence of κ for a selected mixture (with $x_e \approx 0.56$) of each of the four systems studied. Conductivity data presented in Table 6 follow a linear behavior with temperature in the range measured, as it happens for the aqueous mixtures of the same ILs.[3]

From the specific conductivity data at 298.15 K we extract the molar conductivities, Λ, following the usual equation.[29]

$$\Lambda = \kappa/c \qquad (5)$$

The resulting curves are plotted in Figure 4 against concentration in molarity (mol·L^{-1}) and for 298 K. We have fitted the molar conductivity data to an equation derived from Onsager theory[29] that was used previously with good agreement[3,21]

$$\Lambda = \Lambda_0 - D_1\sqrt{c} + D_2 \cdot c \ln c + D_3 \cdot c \qquad (6)$$

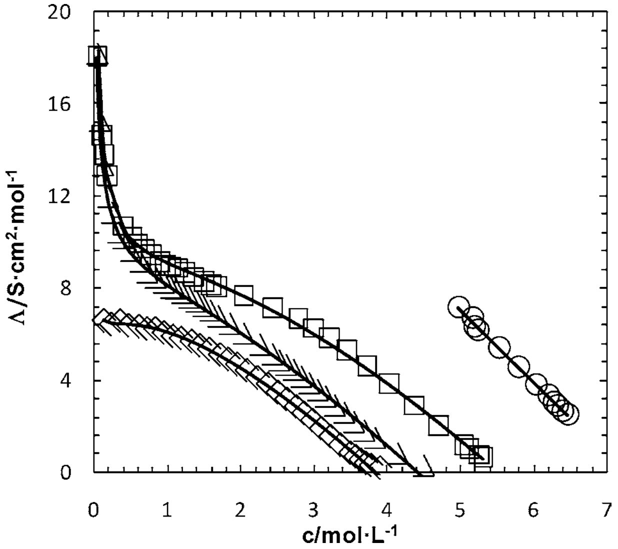

Figure 4. Molar conductivity vs ionic liquid concentration for binary mixtures of ethanol with [EMIM][BF_4] (dot symbols), [BMIM][BF_4] (square symbols), [HMIM][BF_4] (triangle symbols), and [OMIM][BF_4] (rhombus symbols). Lines are the best fit of eq 5 with the parameters given in Table 7.

Table 7. Best Fitting Parameters of Equation 5 Used to Reproduce Molar Conductivity Data

	[EMIM][BF_4]	[BMIM][BF_4]	[HMIM][BF_4]	[OMIM][BF_4]
Λ_0	15.42	24.42	22.98	6.91
D_1	−6.66	44.93	42.39	3.58
D_2	−0.14	8.64	8.36	2.00
D_3	4.88	−29.38	−27.30	−2.73
s	0.08	0.24	0.35	0.10

where Λ_0 is the molar conductivity at infinite dilution and D_i are fitting constants. As observed in Figure 4 the resulting fits reproduce the data with high quality. In Table 7 we include the Λ_0 and D_i fitting parameters for the studied systems, with the corresponding standard deviation, s. The Λ obtained is similar in shape, but about five times lower than that for the [BMIM][BF_4] + water system (the only one common system for both solvents).[3,5] In contrast the D_i parameters are very different, even in sign, which makes it difficult to obtain physical insight from the obtained D_i values.

We have not found any paper reporting electrical conductivity of any system like those measured here.

We have related both transport magnitudes following Walden's rule[29]

$$\Lambda \cdot \eta = K \qquad (7)$$

where K should be a constant at a given temperature in the original formulation of this rule. To do that, we have fitted the conductivity data to a five-grade polynomial equation, so we can obtain the Λ data corresponding exactly to the viscosity concentrations. We estimate that the overall K uncertainty is about 2 % of the obtained value. In Figure 5 we have plotted K against molarity for the four systems. As observed, the K value increases linearly with concentration, similarly in magnitude and shape for all systems. If we compare with the corresponding aqueous systems,[3] we observe that for high concentrations ($c >$ 4 mol·L^{-1}) the K curves agree for both solvents, while for low concentrated mixtures ($c <$ 4 mol·L^{-1}) they diverge. Let us note that K for the systems with water decreases 1 unity from $c =$ 1.5 mol·L^{-1} to 4 mol·L^{-1}, while in ethanol systems it increase

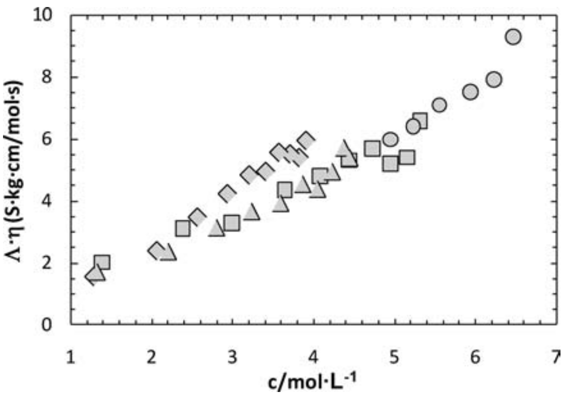

Figure 5. Product of molar conductivity by viscosity multiplied by 104 vs concentration of ethanol for binary mixtures of [EMIM][BF_4] (dot symbols), [BMIM][BF_4] (square symbols), [HMIM][BF_4] (triangle symbols), and [OMIM][BF_4] (rhombus symbols).

3 unities in the same interval. It is not possible analyze *K* quantitatively from its original physical meaning because the mixtures we measure are not those ideal mixtures used to develop Walden's rule,[29] and thus conclusions would be erroneous. In any case, the coincidence of the curves for the four compounds and the observed concordance with the aqueous systems at high ionic liquid concentrations reveals that a physical origin for the *K* behavior must exist.

Conclusions

We measured the two mean transport physical properties (dynamic viscosity and electrical conductivity) in mixtures of four common ionic liquids of the 1-alkyl-3-methyl imidazolium tetrafluoroborate family at four temperatures. The alkyl chains are ethyl, butyl, hexyl, and octyl, the ethyl ionic liquid being only partially miscible with ethanol. From viscosity and conductivity data, we extract viscosity deviations and molar conductivity. Data presented here are original, and we have not found any paper reporting the same experimental data, except for two papers reporting viscosity at 298 K for the system [OMIM][BF_4] + ethanol. Those data have been compared with ours, and both agree within experimental uncertainties.

We multiply the molar conductivity by its viscosity for all mixtures to apply the well-known Walden's rule. Results obtained are common for the four systems, increasing linearly its value with concentration. At high IL concentrations the product obtained for the ethanol systems agrees with those presented before for aqueous systems but not for more diluted ones.

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Received for review July 2, 2010. Accepted September 6, 2010. We thank financial support from Spanish "Ministerio de Educación y Ciencia" with references FIS2007-66823-C02-01 and FIS2007-66823-C02-02, which are partially supported by FEDER funds. Also we thank "Consellería de Industria" from "Xunta de Galicia" for financial support to purchase the visco-densimeter through the IN845B 2009/81-0 project.

JE100687X