Dynamic Viscosities of a Series of 1-Alkyl-3-methylimidazolium Chloride Ionic Liquids and Their Binary Mixtures with Water at Several Temperatures

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Dynamic viscosities, densities, and refractive indices have been measured from $T = 298.15$ K to $T = 343.15$ K for 1-hexyl-3-methylimidazolium chloride, [C$_6$mim][Cl], and 1-methyl-3-octylimidazolium chloride, [C$_8$mim][Cl]. Dynamic viscosities and densities have been determined over the whole composition range for water + [C$_6$mim][Cl] and water + [C$_8$mim][Cl] at $T = (298.15, 313.15, 328.15, \text{and } 343.15)$ K and 0.1 MPa of pressure. Excess molar volumes and viscosity deviations for the binary systems at the above-mentioned temperatures were fitted to a Redlich−Kister equation to determine the fitting parameters and the root mean square deviations. Densities and viscosities of water + 1-butyl-3-methylimidazolium chloride, [C$_4$mim][Cl], at $T = (298.15, 313.15, 328.15, \text{and } 343.15)$ K and 0.1 MPa of pressure have been measured, and apparent molar volumes were determined.

Introduction

Room temperature ionic liquids [RTILs] are emerging as novel solvent replacements for volatile organic compounds traditionally used. Because the ionic liquids are relatively new, experimental measurements of physical properties are extremely scarce but clearly needed.

To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties including viscosity, density, etc. Furthermore, the presence of water in the ionic liquid phase can dramatically affect the physical properties.[1−3] Since it is impossible to measure all the possible combinations of systems, it is necessary to make measurements on selective systems to provide results that can be used to develop correlations and to test predictive methods.

Experimental dynamic viscosity, density, and refractive index data for [C$_6$mim][Cl] and [C$_8$mim][Cl] have been measured from (298.15 to 343.15) K and atmospheric pressure. The results were used to calculate the coefficient of thermal expansion. Experimental dynamic viscosity and density data over the whole composition range for water + [C$_6$mim][Cl] and water + [C$_8$mim][Cl] have been determined at temperatures of (298.15, 313.15, 328.15, and 348.15) K and 0.1 MPa of pressure. The results were used to calculate excess molar volumes and viscosity deviations over the entire mole fraction range for the mixtures.

As [C$_4$mim][Cl] is solid (melting point = 65 °C),[4] experimental dynamic viscosity, density, and refractive index data have not been measured. Experimental dynamic viscosity and density of water + [C$_4$mim][Cl] at $T = (298.15, 313.15, 328.15, \text{and } 343.15)$ K were determined. The results were used to calculate apparent molar volumes.

Experimental Section

Chemicals. [C$_4$mim][Cl], [C$_6$mim][Cl], and [C$_8$mim][Cl] were prepared according to literature procedure,[5,6] and Milli-Q water with 18.2 MΩ electrical conductivity was used.

(*a*) [*C$_4$mim*][*Cl*]. Equal molar amounts of 1-methylimidazole and 1-chlorobutane were added to a two-necked, round-bottomed flask equipped with a reflux condenser, magnetic stirrer, and gas inlet. The reaction mixture was heated under N$_2$ at 343.15 to 353.15 K with stirring between 48 and 72 h depending on the amount of starting materials (the progress of the reaction was monitored by thin-layer chromatography using aluminum sheets silica gel 60 GF-254 and chloroform−10 % methanol as eluent). The resulting viscous liquid was cooled to room temperature, and ethyl acetate (70 mL of ethyl acetate for 0.4 mol of starting 1-chlorobutane) was added with through mixing. The ethyl acetate was decanted and the procedure repeated three times using fresh ethyl acetate. After the last washing, the remaining ethyl acetate was removed by heating under reduced pressure. The ionic liquid obtained was dried by heating (343.15 to 353.15 K) and stirring under high vacuum ($2{\cdot}10^{-1}$ Pa) for 48 h. Yield reaction: 93 %. ^{1}H NMR (400 MHz, D$_2$O, ppm): δ 8.75 [s, 1 H, H-2], 7.52 [s, 1 H, H-4], 7.47 [s, 1 H, H-5], 4.24 [t, $J = 7.1$ Hz, 2 H, NCH_2], 3.93 [s, 3 H, NCH_3], 1.89 [m, 2 H, NCH$_2$CH_2], 1.36 [m, 2 H, NCH$_2$CH$_2$CH_2], 0.96 [t, $J = 7.4$ Hz, 3 H, N(CH$_2$)$_3$CH_3]. Positive FABMS (FISONS VG AUTOSPEC mass spectrometer; glycerol as matrix): mass/charge 315 [(C$_4$mim)$_2$(Cl) + 2]$^+$ (9 %), 313 [(C$_4$mim)$_2$(Cl)]$^+$ (27 %), 140 [(C$_4$mim) + 1]$^+$ (10 %), 139 [C$_4$mim]$^+$ (100 %).

(*b*) [*C$_6$mim*][*Cl*]. The same procedure as that described above for [C$_4$mim][Cl] was followed with the exception of the use of 1-chlorohexane instead of 1-chlorobutane. Yield reaction: 87 %. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 10.55 [s, 1 H, H-2], 7.83 [s, 1 H, H-4], 7.61 [s, 1 H, H-5], 4.34 [t, $J = 7.4$ Hz, 2 H, NCH_2], 4.14 [s, 3 H, NCH_3], 1.93 [m, 2 H, NCH$_2$CH_2], 1.32 [m, 6 H, NCH$_2$CH$_2$(CH_2)$_3$], 0.87 [t, $J = 7.0$ Hz, 3 H, N(CH$_2$)$_5$CH_3]. Positive FABMS (FISONS VG AUTOSPEC mass spectrometer; glycerol as matrix): mass/charge 371 [(C$_6$mim)$_2$(Cl) + 2]$^+$ (10 %), 369 [(C$_6$mim)$_2$(Cl)]$^+$ (28 %), 168 [(C$_6$mim) + 1]$^+$ (12 %), 167 [C$_6$mim]$^+$ (100 %). The water content was $480{\cdot}10^{-6}$ w/w determined by 756 Karl Fisher coulometer.

(*c*) [*C$_8$mim*][*Cl*]. The same procedure as that described above for [C$_4$mim][Cl] was followed with the exception of the use of 1-chlorooctane instead of 1-chlorobutane. Yield reaction: 86 %. ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 10.33 [s, 1 H, H-2], 7.59 [s, 1 H, H-4], 7.37 [s, 1 H, H-5], 4.16 [t, $J = 7.4$ Hz, 2 H,

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Table 1. Density (ρ) and Refractive Index (n_D) of [C$_6$mim][Cl] and [C$_8$mim][Cl] at Several Temperatures

	[C$_6$mim][Cl]		[C$_8$mim][Cl]	
T/K	ρ/g·cm^{-3}	n_D	ρ/g·cm^{-3}	n_D
298.15	1.03967	1.51720	1.00882	1.50987
303.15	1.03681	1.51580	1.00594	1.50838
308.15	1.03396	1.51437	1.00306	1.50689
313.15	1.03113	1.51294	1.00020	1.50543
318.15	1.02830	1.51151	0.99737	1.50396
323.15	1.02549	1.51009	0.99450	1.50250
328.15	1.02269	1.50868	0.99167	1.50103
333.15	1.01989	1.50727	0.98885	1.49956
338.15	1.01711	1.50586	0.98604	1.49810
343.15	1.01432	1.50445	0.98324	1.49664

Table 2. Dynamic Viscosity (η) of [C$_6$mim][Cl] and [C$_8$mim][Cl] at Several Temperatures

	$10^3\eta$/Pa·s	
T/K	[C$_6$mim][Cl]	[C$_8$mim][Cl]
298.15	18089	20883
313.15	3429	4066
328.15	942.1	1091
343.15	339.5	387.2

NCH_2], 3.97 [s, 3 H, NCH_3], 1.75 [m, 2 H, NCH$_2$CH_2)], 1.10 [m, 10 H, NCH$_2$CH$_2$(CH_2)$_5$], 0.70 [t, J = 7 Hz, N(CH$_2$)$_7$CH_3]. Positive FABMS (FISONS VG AUTOSPEC mass spectrometer; glycerol as matrix): mass/charge 427 [(C$_8$mim)$_2$(Cl) + 2]$^+$ (7 %), 425 [(C$_8$mim)$_2$(Cl)]$^+$ (21 %), 196 [(C$_8$mim) + 1]$^+$ (13 %), 195 [C$_8$min]$^+$ (100 %). The water content was 521·10^{-6} w/w determined by 756 Karl Fisher coulometer.

Apparatus and Procedure. Samples were prepared by syringing weighed amounts of the pure liquids into stoppered bottles in a inert-atmosphere glovebox using a Mettler AE-240 Delta Range balance with a precision of ± 10^{-4} g. A glovebox was used because the pure liquids are moisture sensitive.

Densities were measured using an Anton Paar DSA-5000 digital vibrating tube densimeter. Uncertainty and repeatability in density measurement is ± 2·10^{-6} g·cm^{-3} and ± 1·10^{-6}, respectively. The DSA 5000 automatically corrects the influence of viscosity on the measured density.

Refractive indices were determined using an automatic refractometer ABBEMAT-WR Dr. Kernchen with a uncertainty of ± 4·10^{-5}. Kinematic viscosities were determined using an automatic viscosimeter Lauda PVS1 with four Ubbelhode capillary microviscosimeters of 0.4·10^{-3} m, 0.53·10^{-3} m, 0.70·10^{-3} m, and 1.26·10^{-3} m diameter and two Ubbelhode capillary viscosimeters of 4.70·10^{-3} m and 3·10^{-3} m diameter. Gravity fall is the principle of measurement on which this viscosimeter is based. The capillary is maintained in a D20KP LAUDA thermostat with a resolution of 0.01 K. The capillaries are calibrated and credited by the company. The uncertainty of the capillary diameter is ± 0.005 mm. The uncertainty for the viscosimeter has been found to be ± 0.001 mPa·s. The

Table 3. Density (ρ), Excess Molar Volume (V^E), Dynamic Viscosity (η), and Viscosities Deviations ($\Delta\eta$) for Water (1) + [C$_6$mim][Cl] (2) and Water (1) + [C$_8$mim][Cl] (2)

	ρ		$10^3\eta$	$10^3\Delta\eta$		ρ		$10^3\eta$	$10^3\Delta\eta$		ρ		$10^3\eta$	$10^3\Delta\eta$
x_1	g·cm^{-3}	V^E	Pa·s	Pa·s	x_1	g·cm^{-3}	V^E	Pa·s	Pa·s	x_1	g·cm^{-3}	V^E	Pa·s	Pa·s
Water (1) + [C$_6$mim][Cl] (2)														
T = 298.15 K														
0.0000	1.03967	0.000	18089	0.000	0.5594	1.04140	−0.574	201.2	−7748	0.9417	1.01817	−0.113	3.505	−1019
0.1274	1.04045	−0.224	7667	−8129	0.7127	1.03877	−0.469	60.75	−5108	1.0000	0.99703	0.000	0.895	0.000
0.3173	1.04070	−0.373	1020	−11268	0.7830	1.03572	−0.367	33.79	−3929					
0.3906	1.04095	−0.444	499.4	−10597	0.8935	1.02528	−0.154	8.688	−1931					
T = 313.15 K														
0.0000	1.03113	0.000	3429	0.000	0.5594	1.03276	−0.536	88.11	−1431	0.9417	1.00943	−0.045	2.323	−194.8
0.1274	1.03189	−0.216	1746	−1245	0.7127	1.02980	−0.400	30.04	−948.0	1.0000	0.99220	0.000	0.658	0.000
0.3173	1.03222	−0.366	393.5	−1955	0.7830	1.02667	−0.292	17.49	−730.4					
0.3906	1.03263	−0.452	188.9	−1891	0.8935	1.01620	−0.076	5.191	−363.9					
T = 328.15 K														
0.0000	1.02269	0.000	942.1	0.000	0.5594	1.02414	−0.508	44.87	−375.91	0.9417	1.00013	0.012	1.649	−54.158
0.1274	1.02344	−0.214	516.4	−304.55	0.7127	1.02075	−0.340	16.83	−251.99	1.0000	0.98568	0.000	0.519	0.000
0.3173	1.02380	−0.363	165.7	−485.28	0.7830	1.01717	−0.210	10.17	−193.95					
0.3906	1.02430	−0.460	86.76	−477.48	0.8935	1.00679	−0.009	3.367	−98.265					
T = 343.15 K														
0.0000	1.01434	0.000	339.5	0.000	0.5594	1.01540	−0.474	25.37	−126.923	0.9417	0.99026	0.064	1.224	−19.167
0.1274	1.01506	−0.211	207.4	−88.424	0.7127	1.01145	−0.274	10.39	−86.478	1.0000	0.97775	0.000	0.419	0.000
0.3173	1.01550	−0.373	79.07	−156.38	0.7830	1.00771	−0.144	6.542	−67.131					
0.3906	1.01577	−0.440	45.52	−156.98	0.8935	0.99700	0.052	2.358	−34.542					
Water (1) + [C$_8$mim][Cl] (2)														
T = 298.15 K														
0.0000	1.00882	0.000	20883	0.000	0.5334	1.01270	−0.558	921.1	−8824	0.9307	1.00369	−0.031	22.48	−1426
0.1484	1.00961	−0.185	5570	−12214	0.6807	1.01237	−0.442	433.0	−6236	0.9635	1.00110	−0.007	5.714	−756.8
0.2030	1.00999	−0.258	3815	−12829	0.8185	1.00916	−0.192	193.4	−3599	1.0000	0.99703	0.000	0.895	0.000
0.4076	1.01183	−0.510	1325	−11046	0.8803	1.00663	−0.092	80.77	−2420					
T = 313.15 K														
0.0000	1.00020	0.000	4066	0.000	0.5334	1.00376	−0.494	337.9	−1560	0.9307	0.99512	0.032	13.27	−269.2
0.1484	1.00098	−0.177	1470	−1992	0.6807	1.00316	−0.353	175.5	−1123	0.9635	0.99358	0.032	4.248	−144.7
0.2030	1.00135	−0.246	1097	−2144	0.8185	1.00009	−0.113	83.87	−654.9	1.0000	0.99220	0.000	0.658	0.000
0.4076	1.00320	−0.491	387.9	−2021	0.8803	0.99760	−0.015	38.02	−449.4					
T = 328.15 K														
0.0000	0.99167	0.000	1091	0.000	0.5334	0.99481	−0.432	147.7	−361.7	0.9307	0.98589	0.091	8.178	−67.92
0.1484	0.99242	−0.167	484.6	−444.6	0.6807	0.99398	−0.276	83.26	−265.5	0.9635	0.98506	0.068	3.295	−36.99
0.2030	0.99277	−0.231	393.5	−476.1	0.8185	0.99076	−0.038	42.22	−156.3	1.0000	0.98568	0.000	0.519	0.000
0.4076	0.99440	−0.444	170.8	−475.7	0.8803	0.98816	0.059	20.45	−110.6					
T = 343.15 K														
0.0000	0.98324	0.000	387.2	0.000	0.5334	0.98596	−0.385	74.31	−106.6	0.9307	0.97615	0.146	5.329	−21.90
0.1484	0.98387	−0.146	200.1	−129.7	0.6807	0.98480	−0.209	44.23	−79.69	0.9635	0.97571	0.103	2.647	−11.88
0.2030	0.98421	−0.210	165.4	−143.3	0.8185	0.98111	0.041	24.22	−46.42	1.0000	0.97775	0.000	0.419	0.000
0.4076	0.98560	−0.394	84.75	−144.8	0.8803	0.97839	0.129	12.17	−34.56					

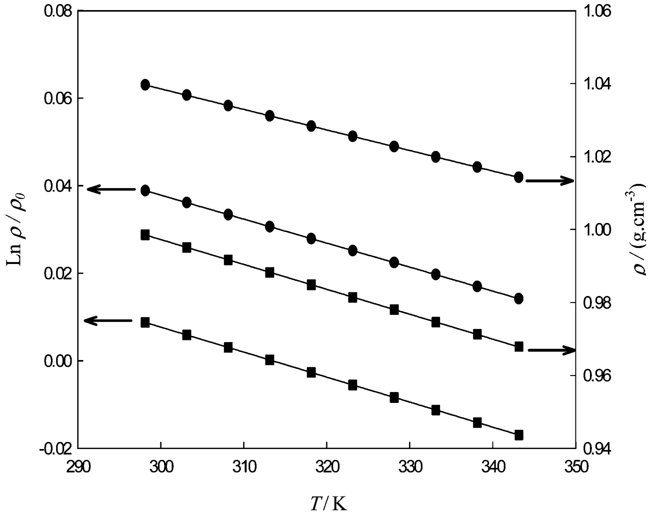

Figure 1. Experimental values of ln ρ/ρ_0 and ρ for ●, [C$_6$mim][Cl]; and ■, [C8mim][Cl] plotted against temperature and fitted lines. For [C$_6$mim][Cl]: ln $\rho/\rho_0 = 0.2024 - 5 \cdot 10^{-4}\ T$/K and ρ/g·cm^{-3} = $1.2075 - 6 \cdot 10^{-4}$ T/K. For [C$_8$mim][Cl]: ln $\rho/\rho_0 = 0.2179 - 6 \cdot 10^{-4}\ T$/K and ρ/g·cm^{-3} = $1.1783 - 6 \cdot 10^{-4}\ T$/K.

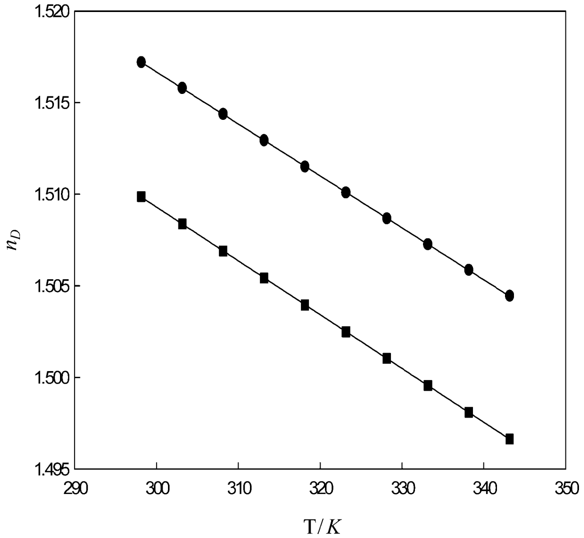

Figure 2. Experimental values of n_D for ●, [C$_6$mim][Cl]; and ■, [C8mim][Cl] are plotted against temperature and fitted lines. For [C$_6$mim][Cl]: $n_D = 1.6018 - 3 \cdot 10^{-4}$ T/K. For [C$_8$mim][Cl]: $n_D = 1.5974 - 3 \cdot 10^{-4}$ T/K.

equipment has a control unit PVS1 (processor viscosity system) that is a PC-controlled instrument for the precise measurement of fall time, using standardized glass capillaries, with an uncertainty of 0.01 s.

Results and Discussion

Pure Components. Dynamic viscosity, density, and refractive index for the [C$_6$mim][Cl] and [C$_8$mim][Cl from 298.15 K to 343.15 K and atmospheric pressure are reported in Tables 1 and 2. It can be observe in than the density, viscosity, and refractive index decrease as the temperature increase, this decrease being more notorious at low temperature.

The ln ρ/ρ_0, where ρ_0 is 1 g·cm^{-3}, and ρ of ionic liquids against temperature are represented in Figure 1. The values were fitted by the least-squares method. The correlation coefficient for ln ρ and ρ are ≈ 1 for [C$_6$mim][Cl] and [C$_8$mim][Cl]. The coefficient of thermal expansion is defined by the following equation:

$$\alpha \equiv 1/v(\partial V/\partial T)_p = -(\partial \ln \rho/\partial T)_p \qquad (1)$$

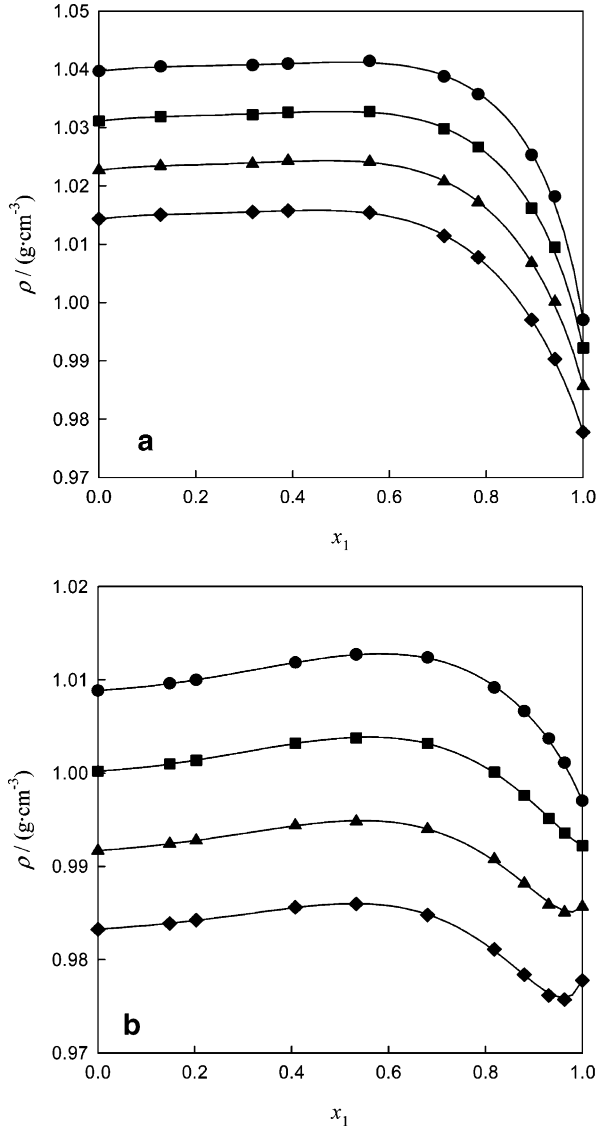

Figure 3. Densities, ρ, plotted against mole fraction at ●, T = 298.15 K; ■, T = 313.15 K; ▲, T = 328.15 K; and ◆, T = 343.15 K for the binary mixtures (a) water (1) + [C$_6$mim][Cl] (2), (b) water (1) + [C$_8$mim][Cl] (2), and fitted curves (—) using the Redlich−Kister parameters.

where α is the coefficient of thermal expansion, V is the molar volume of the ionic liquid, and ρ is the density. Values of $\alpha = 5 \cdot 10^{-4}$ for [C$_6$mim][Cl] and $\alpha = 6 \cdot 10^{-4}$ for [C$_8$mim][Cl] were obtained from this equation and represented in Figure 1. These values of α are very similar for both ionic liquids. In Figure 1, it can be seen that the density decreases as in the following sequence: [C$_6$mim][Cl] > [C$_8$mim][Cl].

Figure 2 shows the experimental values of refractive index for [C$_6$mim][Cl] and [C$_8$mim][Cl] against temperature. The values were fitted by the least-squares method. The correlation coefficient is 0.9999 for [C$_6$mim][Cl] and [C$_8$mim][Cl]. We can observe that the density and refractive index decrease as in the following sequence: [C$_6$mim][Cl] > [C$_8$mim][Cl].

Binary Systems. Dynamic viscosity, density, excess molar volume, and viscosity deviation for water + [C$_6$mim][Cl] and water + [C$_8$mim][Cl] at temperatures of (298.15, 313.15, 328.15, and 343.15) K and 0.1 MPa of pressure are listed in Table 3. In Figures 3 and 4, we can observe densities and viscosities experimental data and the correlation curve using the Redlich−Kister parameters. In Figure 3, we can see that the densities of [C$_6$mim][Cl] are higher than densities of [C$_8$mim][Cl] for all temperatures. In both systems, we can observe that the density

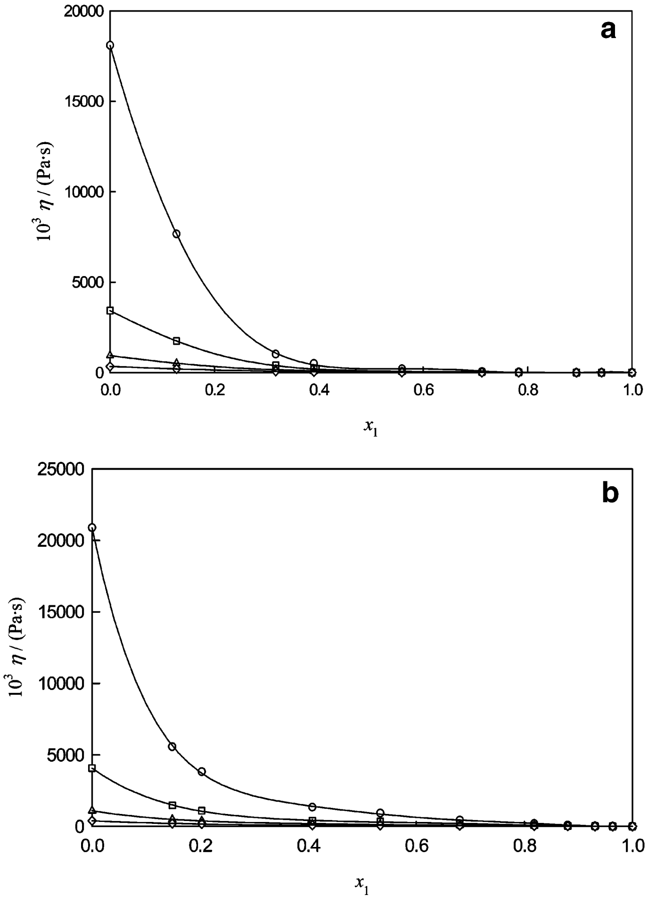

Figure 4. Viscosities, η, plotted against mole fraction at ○, T = 298.15 K; □, T = 313.15 K; △, T = 328.15 K; and ◇, T = 343.15 K for the binary mixtures (a) water (1) + [C_6mim][Cl] (2), (b) water (1) + [C_8mim]-[Cl] (2), and fitted curves (—) using the Redlich−Kister parameters.

Table 4. Fitting Parameters and Root Mean Square Deviations (σ) for Water (1) + [C_6mim][Cl] (2) and Water (1) + [C_8mim][Cl] (2)

	B_0	B_1	B_2	B_3	B_4	σ
Water (1) + [C_6mim][Cl] (2)						
T = 298.15 K						
V^E/cm^3·mol^{-1}	−2.1122	−1.0469	0.3695	1.9572		0.016
$10^{-3}\ \Delta\eta$/Pa·s	−35293	35977	−29395	−1697.4	14893	36.099
T = 313.15 K						
V^E/cm^3·mol^{-1}	−2.0529	−0.7101	1.0058	2.2032		0.012
$10^{-3}\ \Delta\eta$/Pa·s	−6468.6	6057.2	−3770.2	−2111.1	3233.3	5.471
T = 328.15 K						
V^E/cm^3·mol^{-1}	−1.9988	−0.3932	1.5263	2.5081		0.011
$10^{-3}\ \Delta\eta$/Pa·s	−1678.6	1377.0	−663.88	−440.67	490.43	4.438
T = 343.15 K						
V^E/cm^3·mol^{-1}	−1.9145	−0.0402	1.9581	2.5653		0.006
$10^{-3}\ \Delta\eta$/Pa·s	−562.65	423.03	−153.12	−246.21	212.32	2.022
Water (1) + [C_8mim][Cl] (2)						
T = 298.15 K						
V^E/cm^3·mol^{-1}	−2.2263	−0.2382	1.9222	0.9555		0.004
$10^{-3}\ \Delta\eta$/Pa·s	−37809	33603	−33347	36577	−21989	51.279
T = 313.15 K						
V^E/cm^3·mol^{-1}	−2.0378	0.2145	2.2894	0.9311		0.004
$10^{-3}\ \Delta\eta$/Pa·s	−6812.8	6496.7	−5771.4	3009.4	−1119.4	20.415
T = 328.15 K						
V^E/cm^3·mol^{-1}	−1.8091	0.3780	2.5152	1.4113		0.006
$10^{-3}\ \Delta\eta$/Pa·s	−1598.1	1504.8	−1192.1	398.56	−233.00	7.416
T = 343.15 K						
V^E/cm^3·mol^{-1}	−1.6108	0.4791	2.8600	1.8843		0.005
$10^{-3}\ \Delta\eta$/Pa·s	−477.86	499.27	−420.73	−27.613	82.745	2.429

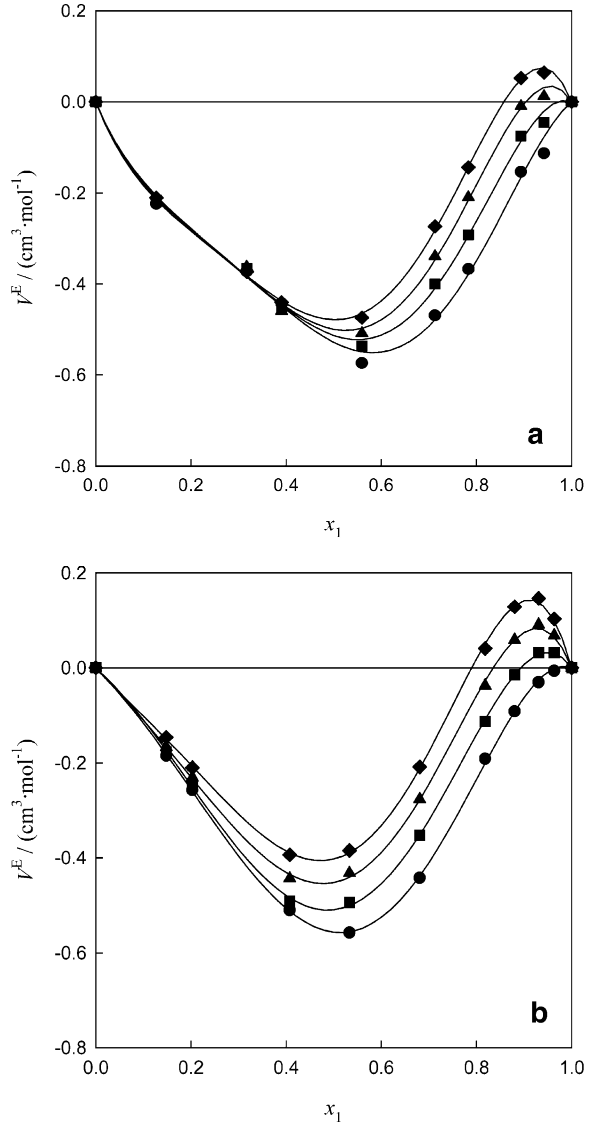

Figure 5. Excess molar volume, V^E, from the Redlich−Kister equation plotted against mole fraction at ●, T = 298.15 K; ■, T = 313.15 K; ▲, T = 328.15 K; and ◆, T = 343.15 K for the binary mixtures (a) water (1) + [C_6mim][Cl] (2) and (b) water (1) + [C_8mim][Cl] (2).

decreases as the temperature increases. The system [C_6mim]-[Cl] + water presents a maximum at a mole fraction of approximately 0.55 for all temperatures. The system [C_8mim]-[Cl] + water presents a maximum at a mole fraction of about 0.55 for four studied temperatures and a minimum at a mole fraction of approximately 0.9 for 328.15 K and 343.15 K.

As can be seen in Figure 4, the viscosity of [C_8mim][Cl] is higher than the viscosity of [C_6mim][Cl]; the viscosity decreases with temperature for all temperatures. These figures show the great variations of viscosity depending on the water content at all the studied temperatures. A small quantity of water causes a great viscosity decrease, although the density is not affected as much.

The excess molar volumes and viscosity deviation are calculated by the following equations:

$$V^E = \sum_{i=1}^{N} x_i M_i(\rho^{-1} - \rho_i^{-1}) \tag{2}$$

$$\Delta\eta = \eta - \sum_{i}^{N} x_i \eta_i \tag{3}$$

where ρ and ρ_i are the density of the mixture and the density of

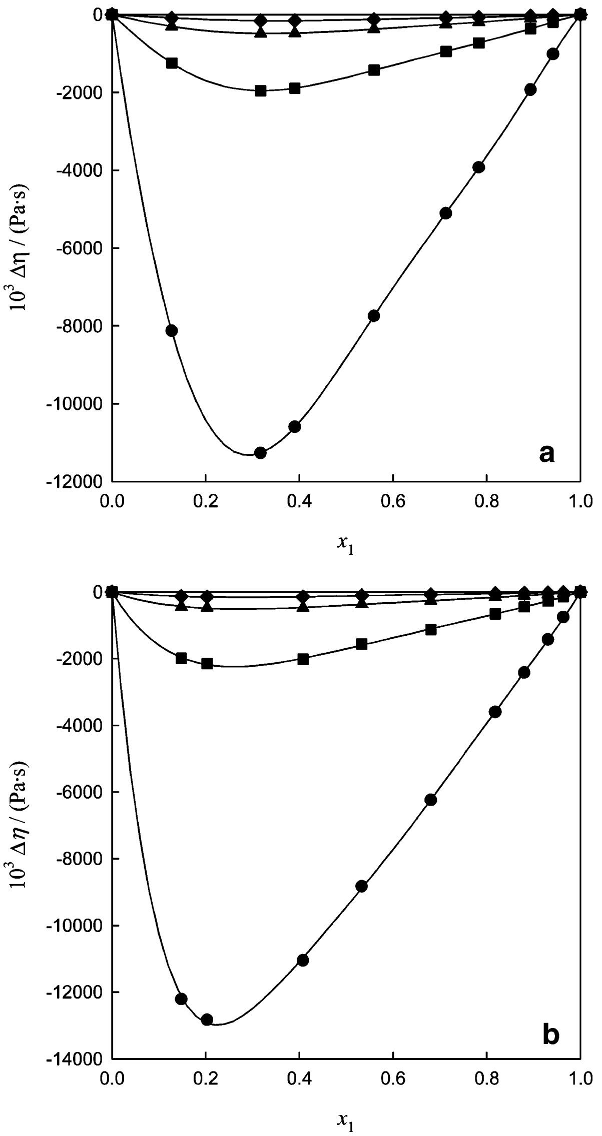

Figure 6. Viscosities deviations, $\Delta\eta$, from the Redlich−Kister equation plotted against mole fraction at ●, T = 298.15 K; ■, T = 313.15 K; ▲, T = 328.15 K; and ◆, T = 328.15 K for the binary mixtures (a) water (1) + [C$_6$mim][Cl] (2) and (b) water (1) + [C$_8$mim][Cl] (2).

the pure components, respectively; x_i represents the mole fraction of the i component; and η and η_i are the dynamic viscosity of the mixture and the pure component, respectively.

The binary deviations at several temperatures were fitted to a Redlich−Kister[7] type equation:

$$\Delta Q_{ij} = x_i x_j \sum_{p=0}^{M} B_p (x_i - x_j)^p \qquad (4)$$

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 polynomic expansion, which was optimized using the F-test.[8] The fitting parameters are given in Table 4 together with the root mean square deviations. They are calculated from the values of the experimental and calculated property and the number of experimental data, represented by z_{exp}, z_{calc}, and n_{dat}, respectively:

$$\sigma = \{\sum_{i}^{n_{\mathrm{dat}}} (z_{\mathrm{exp}} - z_{\mathrm{calc}})^2 / n_{\mathrm{dat}}\}^{1/2} \qquad (5)$$

Table 5. Density (ρ), Molalities (M), Apparent Molar Volume (V_Φ), and Dynamic Viscosity (η) of Water (1) + [C$_4$mim][Cl] (2)

x_1	ρ/g·cm^{-3}	m	V_Φ	$10^3\eta$/Pa·s
		T = 298.15 K		
0.5666	1.0810	42.46	159.77	123.5
0.6070	1.0799	35.94	159.62	72.16
0.6933	1.0765	24.56	159.26	35.66
0.7698	1.0711	16.60	158.91	18.08
0.8279	1.0638	11.53	158.76	10.19
0.8674	1.0571	8.489	158.54	6.628
0.9194	1.0423	4.868	158.65	3.543
0.9625	1.0223	2.163	159.42	1.886
0.9885	1.0052	0.648	161.21	1.175
		T = 313.15 K		
0.5666	1.0720	42.46	161.19	56.63
0.6070	1.0708	35.94	161.08	35.36
0.6933	1.0672	24.56	160.81	18.94
0.7698	1.0615	16.60	160.60	10.11
0.8279	1.0541	11.53	160.59	6.125
0.8674	1.0471	8.489	160.60	4.123
0.9194	1.0328	4.868	161.01	2.311
0.9625	1.0140	2.163	162.26	1.297
0.9885	0.9991	0.648	164.11	0.955
		T = 328.15 K		
0.5666	1.0634	42.46	162.53	30.04
0.6070	1.0620	35.94	162.46	19.75
0.6933	1.0581	24.56	162.27	11.32
0.7699	1.0521	16.60	162.18	6.474
0.8279	1.0445	11.53	162.29	4.019
0.8674	1.0373	8.489	162.46	2.795
0.9194	1.0233	4.868	163.05	1.635
0.9625	1.0061	2.163	164.11	0.955
0.9885	0.9893	0.648	170.85	0.753
		T = 343.15 K		
0.5666	1.0547	42.46	163.87	17.69
0.6070	1.0531	35.94	163.85	12.20
0.6933	1.0488	24.56	163.74	7.386
0.7699	1.0424	16.60	163.76	4.419
0.8279	1.0344	11.53	164.02	2.858
0.8674	1.0271	8.489	164.29	2.043
0.9194	1.0131	4.868	165.10	1.228
0.9625	0.9967	2.163	166.28	0.741
0.9885	0.9796	0.648	175.35	0.652

Figures 5 and 6 show the fitted curves as well as excess and viscosity deviations values for binary mixtures: water + [C$_6$mim][Cl] and water + [C$_8$mim][Cl] at T = (298.15, 313.15, 328.15, and 343.15) K. In Figure 5. we can observe that the excess molar volumes presents a minimum at $x \approx 0.55$ and a maximum at $x \approx 0.95$ for the two systems. The minimum decreases and the maximum increases as temperature increases; this behavior can be explained because hydrogen bonding is certainly more T-dependent (becoming negligible at high temperatures) than Coulombic interactions. This result agrees with the work of Rebelo et al.[9] The minimum can be due to hydrogen bonds between water molecules and ionic liquids. At higher concentrations of water, we can observe a maximum due to the dissociation of the ions forming the ionic liquids. This behavior agrees with study done by Miki et al.[10] In Figure 6, for viscosity deviations, the sign is negative for all the binary systems, and the minima lie at a mole fraction of approximately 0.3 for water + [C$_6$mim][Cl] and at a mole fraction of about 0.2 for water + [C$_8$mim][Cl]. The viscosity deviations decrease as the temperature increases; this behavior is similar for both systems.

Water + [C$_4$mim][Cl] was prepared from [C$_4$mim][Cl] saturated in water (9.65 % w/w). The experimental values of density, molality, apparent molar volume, and viscosity of water + [C$_4$mim][Cl] at T = (298.15, 313.15, 328.15, and 343.15) K and atmospheric pressure are given in Table 5. In this table, we can observe that the viscosity decreases as the water content increases.

The apparent molar volumes, V_Φ, were determine from the solution densities using the following equation:

$$V_\Phi = \frac{M_{\mathrm{w}}}{\rho} - 1000\frac{(\rho - \rho_0)}{(\rho\rho_0 m)} \qquad (6)$$

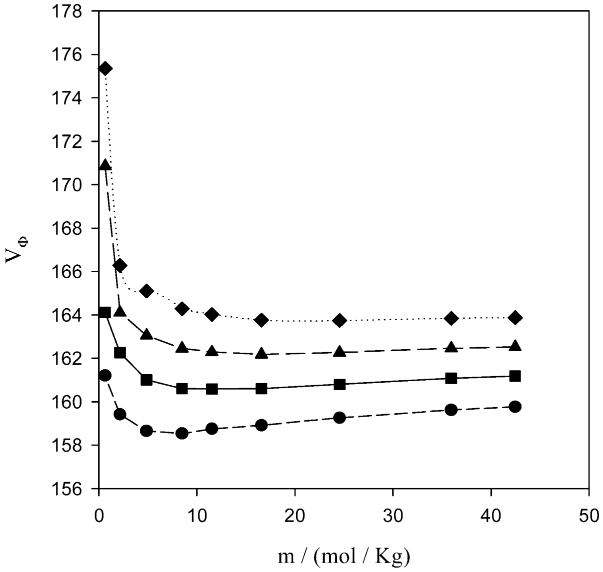

Figure 7. Apparent molar volumes plotted against molalities at ●, T = 298.15 K; ■, T = 313.15 K; ▲, T = 328.15 K; and ◆, T = 328.15 K for the binary mixture water (1) + $[C_4mim][Cl]$ (2).

where M_w is the molecular weight of the solute; m is the molality; and ρ_0 and ρ are the densities of the solvent and the solution, respectively. In Figure 7, we can observe that the apparent molar volume presents a minimum at 10 m and shows a very small temperature effect in the range of 298.15 to 343.15 K.

Conclusions

In this paper we present values of density, viscosity, and refractive index of $[C_6mim][Cl]$ and $[C_8mim][Cl]$ from 298.15 K to 343.15 K and atmospheric pressure. We can observe that the density and refractive index are lower for $[C_6mim][Cl]$ than for $[C_8mim][Cl]$.

In this work, dynamic viscosities and densities of the binary systems water + $[C_6mim][Cl]$ and water + $[C_8mim][Cl]$ at T = (298.15, 313.15, 328.15, and 348.15) K and atmospheric pressure, over the whole composition range, have been determined. Viscosity is more sensitive to the water content than density.

The excess molar volumes and viscosity deviations for these binary systems were determined from experimented data. These data were fitted to Redlich−Kister equation to test the quality of the experimental values.

Values of density and viscosity of water with $[C_4mim][Cl]$ were measured at T = (298.15, 313.15, 328.15, and 348.15) K and atmospheric pressure. Apparent molar values were calculated from experimental data.

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