JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

pubs.acs.org/jced

Densities and Viscosities of 1-Ethyl-3-methylimidazolium *n*-Alkyl Sulfates

Anabela J. L. Costa, José M. S. S. Esperança,* Isabel M. Marrucho,* and Luís Paulo N. Rebelo

Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. República, 2780-157 Oeiras, Portugal

ABSTRACT: Density and viscosity data for four 1-ethyl-3-methylimidazolium-based ionic liquids combined with alkyl sulfate, $[C_nSO_4]^-$ with $n = 1, 4, 6$, and 8, and hydrogen sulfate, $[HSO_4]^-$, anions were measured at atmospheric pressure in the temperature range $283 < T/K < 363$. Isobaric thermal expansion coefficients were calculated from the density results. This work studies the effect of increasing the alkyl chain length of the sulfate-based anion on the density, viscosity, and related properties of this family of ionic liquids. The effective volumes of the distinct anions used were calculated from the measured density values, simply by subtracting the effective volume of the cation already available from literature to the molar volume of the ionic liquid. We also evaluated the predictive ability of group contribution methods for density and viscosity. Since large deviations between the predictions and the experimental data occurred for both density and viscosity, new group contribution parameters were proposed. The results clearly show that $[HSO_4]^-$ cannot be considered part of the $[C_nSO_4]^-$ family.

■ INTRODUCTION

Ionic liquid (IL) research has boomed due to attractive properties common to several families of ILs, such as wide liquid range, nonflammability, and negligible vapor pressure at ambient conditions.[1−4] The potential development of reliable and economical process designs for industrial applications of ILs depends on the thorough knowledge of their most relevant thermophysical properties such as density,[5−7] viscosity,[8] and heat capacity.[9] Although the literature in this area has grown enormously in the past few years, every day new ILs are being synthesized. A careful analysis of the literature shows that the basic properties have only been measured for a limited number of ILs. The IL Thermo database contains no information regarding the density and viscosity data for the ILs used in this work, namely, $[C_2mim][C_nSO_4]$ with $n = 1, 4, 6$, and 8 and $[C_2mim][HSO_4]$. However, for the more common $[C_2mim][C_2SO_4]$ several studies have been published.

Generally, IL density varies between $0.85\ g \cdot cm^{-3}$ and $1.6\ g \cdot cm^{-3}$, depending on the choice of both cation and anion; it then decreases as the alkyl side chain grows in a systematic way.[10] The viscosity of room temperature IL ranges from 10 cP to 10^5 cP, which is up to 3 orders of magnitude higher than that of conventional organic solvents. Such high viscosities are known to severely hinder possible industrial applications. Impurities such as water are important, since they dramatically reduce the IL viscosity.[11] Commonly, the increase of the alkyl chain length of the $[C_nmim]^+$ cation increases the viscosity due to an increase in the van der Waals interaction domains.[8] Although considerable data exist relating to the influence of increasing the alkyl side chain in alkyl-imidazolium based ILs, few systematic studies have appeared on the same effect in the anion. In fact, there are few anions where this effect can be evaluated. One such case is the previously studied 1-alkyl-3-methylimidazolium alkyl sulfonate family.[12,13] Another example is the 1-alkyl-3-methylimidazolium alkyl sulfate family, for which only two density studies for ILs with alkyl chain longer than the ethyl group[14,15] were found. Other papers only show disparate data for the other members of family.[16,17] Viscosity data are even more scarce.[15]

This work investigates the relationship between densities, viscosities, and ionic structures, to establish principles for the molecular design of ILs. To that end, 1-ethyl-3-methylimidazolium was always used as the cation, while the anion alkyl chain length of the sulfate anion, $[C_nSO_4]^-$, changed from $n = 1, 4, 6$, and 8. The $[HSO_4]^-$ is also studied. Results from this same laboratory for $[C_2mim][C_2SO_4]$ are used to analyze the alkyl chain influence on the thermophysical properties.[18,19] We have also recently studied ILs of the family $[C_nmim][C_mSO_3]$,[12,13] and we briefly compare the density and viscosity data for both. Group contribution models[20−24] are tested in the prediction of the density and the viscosity of the 1-ethyl-3-methylimidazolium alkyl sulfate family of ILs and new group parameters are proposed.

■ EXPERIMENTAL SECTION

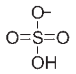
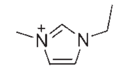
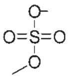
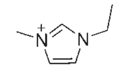
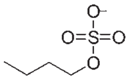
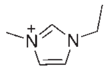
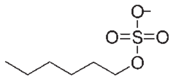
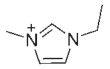
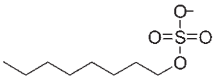
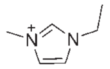
Chemicals. The ILs studied share a common cation, 1-ethyl-3-methylimidazolium, and the anion is either hydrogen sulfate or belongs to the alkyl sulfate family. Table 1 lists the ILs, their respective acronyms, and chemical structure. The suppliers, purity, and NMR analysis appear in Table 2.

To reduce water and volatile compounds to negligible values, all samples were dried under vacuum (0.1 Pa) and vigorously stirred at moderate temperature (330 K) for at least one day immediately before use. Coulometric Karl Fischer titrations revealed very low levels of water, always below 100 ppm.

Methods and Procedure. *Densimeter.* The density measurements were performed at atmospheric pressure with an Anton Paar vibrating tube densimeter, model DMA 5000, at temperatures ranging from (293 to 363) K. The densimeter was internally calibrated by measuring the densities of atmospheric air and bidistilled water, according to manufacturer recommendations. The DMA 5000 cell is embedded in a cavity inside a metal block, controlled for temperature by several Peltier units resulting in a

Received: May 5, 2011
Accepted: July 10, 2011
Published: July 22, 2011

Table 1. Acronyms and Chemical Structure of the ILs Used in This Work

Ionic Liquid	Acronym	Anion	Cation
1-ethyl-3-methylimidazolium hydrogen sulfate	$[C_2mim][HSO_4]$		
1-ethyl-3-methylimidazolium methyl sulfate	$[C_2mim][C_1SO_4]$		
1-ethyl-3-methylimidazolium butyl sulfate	$[C_2mim][C_4SO_4]$		
1-ethyl-3-methylimidazolium hexyl sulfate	$[C_2mim][C_6SO_4]$		
1-ethyl-3-methylimidazolium octyl sulfate	$[C_2mim][C_8SO_4]$		

temperature stability better than ± 2 mK for periods over 10 min. Under these operating conditions, the density measurement repeatability was better than 0.04 $kg\cdot m^{-3}$, and the expanded uncertainty was estimated to be ± 0.3 $kg\cdot m^{-3}$. All reported density data were corrected for the viscosity effect using the internal calibration of the densimeter.

To prevent any contamination by water or air bubbles, we filled a syringe with (ca. 2 cm^3) of the liquid under nitrogen flow and injected it into the densimeter. Three replicas were measured at 293 K, and if the density agreed up to 0.04 $kg\cdot m^{-3}$, the last sample was used to measure the density for the entire temperature range.

Viscometer. Measurements of viscosity were performed using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The device uses Peltier elements for fast and efficient thermostatization. The temperature uncertainty is ± 0.02 K. The precision of the dynamic viscosity measurements is ± 0.5 %. The overall uncertainty of the measurements (taking into account the purity and handling of the samples) is estimated to be 2 %.[8]

Measurements were carried out at temperatures between (283.15 and 373.15) K at atmospheric pressure. At least three measurements were performed for each IL, and the reported result is the average value with a mean deviation smaller than 1.0 %.

RESULTS AND DISCUSSION

Density. Table 3 presents the experimental density data at atmospheric pressure for $[C_2mim][HSO_4]$, $[C_2mim][C_1SO_4]$, $[C_2mim][C_4SO_4]$, $[C_2mim][C_6SO_4]$, and $[C_2mim][C_8SO_4]$ as well as, for comparison purposes, the density data for 1-ethyl-3-methylimidazolium ethyl sulfate from the literature.[18] Figure 1 illustrates the experimental density at atmospheric pressure as a function of temperature for this IL family. The density data behaved as expected with a systematic fall as the alkyl side chain of the anion increased, with values between 1.366 $g\cdot cm^{-3}$ and 1.096 $g\cdot cm^{-3}$ at 298.15 K. Moreover, the $[C_2mim][C_nSO_4]$ density is higher than that of $[C_2mim][C_nSO_3]$ for comparable alkyl chain lengths of the anion.[12]

To the best of our knowledge, only four studies[14−17] present experimental density data for $[C_2mim][HSO_4]$, $[C_2mim][C_1SO_4]$, $[C_2mim][C_4SO_4]$, $[C_2mim][C_6SO_4]$, or $[C_2mim][C_8SO_4]$. For $[C_2mim][HSO_4]$ the data available[17] are in excellent agreement with ours, with deviations within the experimental uncertainty. In the case of $[C_2mim][C_1SO_4]$ two data sets are available.[16,17] Ficke et al. present results about 0.14 % higher than ours, once again in excellent agreement. The data from Shekaari et al. are about 3 % to 6 % higher than ours, and the temperature trend with temperature is completely distinct. For $[C_2mim][C_4SO_4]$, $[C_2mim][C_6SO_4]$, and $[C_2mim][C_8SO_4]$ two experimental sets of density data[14,15] are available. Russina et al. only present the fitting parameters for the linear temperature dependence of density from (283.15 to 333.15) K. These tendencies are in close agreement with ours, with deviations smaller than 0.02 % for $[C_2mim][C_4SO_4]$ and $[C_2mim][C_6SO_4]$ and less than 0.1 % for $[C_2mim][C_8SO_4]$. Himmler et al. only present one density datum for each IL at room temperature. The results fit perfectly within the uncertainty of our measurements.

Isobaric Thermal Expansion Coefficient. This second-order thermodynamic function was safely derived by considering exclusive density values corresponding to IL viscosities below 600 $mPa\cdot s$; the internal equipment correction to account for higher viscosities might have led to erroneous results. In practice, this means that all density data points were used in the cases of $[C_2mim][C_1SO_4]$, $[C_2mim][C_4SO_4]$, and $[C_2mim][C_6SO_4]$, while for $[C_2mim][HSO_4]$ and $[C_2mim][C_8SO_4]$ only data points at temperatures higher than (310 and 297) K, respectively, were considered.

For all ILs, a simple first-order polynomial is insufficient to fit the data over the temperature range studied. Thus, a second-order polynomial equation was used to fit the ln ρ versus T data (eq 1), and the parameters obtained allow for the calculation of the corresponding (α_p) values (eq 2).

$$\ln(\rho/kg\cdot m^{-3}) = A + B(T/K) + C(T/K)^2 \qquad (1)$$

Table 2. IL Specifications and NMR Analysis

IL	$M/\mathrm{g\cdot mol^{-1}}$	supplier	purity/%	^{1}H NMR spectroscopy (400 MHz, DMSO-d^6) δ
$[C_2mim][HSO_4]$	208.24	Io-li-tec	99	1.42 (t, 3H, J = 7.32 Hz, $NCH_2\mathbf{CH_3}$) 3.86 (s, 3H, $N\mathbf{CH_3}$) 4.20 (q, 2H, J = 3.32 Hz, $N\mathbf{CH_2}CH_3$) 7.71 (dd, 1H, J = 1.44 Hz, $C(5)\mathbf{H}$) 7.80 (dd, 1H, J = 1.44 Hz, $C(4)\mathbf{H}$) 9.16 (s, 1H, $C(2)\mathbf{H}$)
$[C_2mim][C_1SO_4]$	222.26	Io-li-tec	99	1.42 (t, 3H, J = 7.28 Hz, $NCH_2\mathbf{CH_3}$) 3.38 (s, 3H, $SO_4\mathbf{CH_3}$) 3.86 (s, 3H, $N\mathbf{CH_3}$) 4.20 (q, 2H, J = 7.28 Hz, $N\mathbf{CH_2}CH_3$) 7.71 (dd, 1H, J = 3.60 Hz, $C(5)\mathbf{H}$) 7.79 (dd, 1H, J = 3.60 Hz, $C(4)\mathbf{H}$) 9.12 (s, 1H, $C(2)\mathbf{H}$)
$[C_2mim][C_4SO_4]$	264.34	Merck	98	0.88 (t, 3H, J = 7.36 Hz, $SO_4CH_2CH_2CH_2\mathbf{CH_3}$) 1.31 (m, 2H, $SO_4CH_2CH_2\mathbf{CH_2}\ CH_3$) 1.43 (t, 3H, J = 7.32 Hz, $NCH_2\mathbf{CH_3}$) 1.48 (qt, 2H, J = 7.68 Hz, $SO_4CH_2\mathbf{CH_2}CH_2\ CH_3$) 3.70 (t, 2H, J = 6.68 Hz, $SO_4\mathbf{CH_2}CH_2CH_2\ CH_3$) 3.86 (s, 3H, $N\mathbf{CH_3}$) 4.20 (q, 2H, J = 7.28 Hz, $N\mathbf{CH_2}CH_3$) 7.71 (dd, 1H, J = 1.72 Hz, $C(5)\mathbf{H}$) 7. 80 (dd, 1H, J = 1.72 Hz, $C(4)\mathbf{H}$) 9.13 (s, 1H, $C(2)\mathbf{H}$)
$[C_2mim][C_6SO_4]$	292.39	Merck	98	0.88 (t, 3H, J = 7.04 Hz, $SO_4CH_2CH_2(CH_2)_3\mathbf{CH_3}$) 1.28 (m, 6H, $SO_4CH_2CH_2(\mathbf{CH_2})_3CH_3$) 1.42 (t, 3H, J = 7.32 Hz, $NCH_2\mathbf{CH_3}$) 1.49 (qt, 2H, J = 7.24 Hz, $SO_4CH_2\mathbf{CH_2}(CH_2)_3CH_3$) 3.68 (t, 2H, J = 6.64 Hz, $SO_4\mathbf{CH_2}CH_2(CH_2)_3CH_3$) 3.86 (s, 3H, $N\mathbf{CH_3}$) 4.19 (q, 2H, J = 7.32 Hz, $N\mathbf{CH_2}CH_3$) 7.71 (dd, 1H, J = 1.56 Hz, $C(5)\mathbf{H}$) 7.79 (dd, 1H, J = 1.56 Hz, $C(4)\mathbf{H}$) 9.12 (s, 1H, $C(2)\mathbf{H}$)
$[C_2mim][C_8SO_4]$	320.45	Merck	98	0.87 (t, 3H, J = 6.96 Hz, $SO_4CH_2CH_2(CH_2)_3\mathbf{CH_3}$) 1.27 (m, 10H, $SO_4CH_2CH_2(\mathbf{CH_2})_5CH_3$) 1.42 (t, 3H, J = 7.32 Hz, $NCH_2\mathbf{CH_3}$) 1.49 (qt, 2H, J = 6.96 Hz, $SO_4CH_2\mathbf{CH_2}(CH_2)_5CH_3$) 3.68 (t, 2H, J = 6.64 Hz, $SO_4\mathbf{CH_2}CH_2(CH_2)_5CH_3$) 3.84 (s, 3H, $N\mathbf{CH_3}$) 4.19 (q, 2H, J = 7.28 Hz, $N\mathbf{CH_2}CH_3$) 7.69 (dd, 1H, J = 3.56 Hz, $C(5)\mathbf{H}$); 7.78 (dd, 1H, J = 3.56 Hz, $C(4)\mathbf{H}$) 9.15 (s, 1H, $C(2)\mathbf{H}$)

where A, B, and C are fitting parameters and T is the temperature in K.

The A, B, and C parameters for each IL, as well as the respective standard deviation, appear in Table 4.

The isobaric thermal expansion coefficient, α_p, can be defined as the derivative of ln ρ to temperature as expressed in eq 2.

$$\alpha_p(K^{-1}) = -\left(\frac{\partial \ln \rho(\mathrm{kg\cdot m^{-3}})}{\partial T(\mathrm{K})}\right)_p \qquad (2)$$

The isobaric thermal expansion coefficients for this family of ILs appear in Figure 2. The use of a second-order polynomial function is warranted by the intrinsic precision along the densimetry runs, determined using an apparatus that allows for the measurement of density with 5 significant digits, corresponding to 0.001 % deviations. It must be stressed, however, that the overall uncertainty of the density measurements is estimated to be much higher (around 0.02 %) due to problems associated with the full characterization of the samples regarding their purity. The corresponding estimated overall uncertainty in the values of

Table 3. Experimental Density Data, ρ/kg·m^{-3}, of ILs with a Common Cation 1-Ethyl-3-methylimidazolium, $[C_2mim]^+$, and Distinct Alkyl Sulfate and Hydrogen Sulfate Anions, from (293.15 to 363.15) K at Atmospheric Pressure

	ρ/kg·m^{-3}					
T/K	$[HSO_4]^-$	$[C_1SO_4]^-$	$[C_2SO_4]^-$[18]	$[C_4SO_4]^-$	$[C_6SO_4]^-$	$[C_8SO_4]^-$
293.15	1368.86	1289.48	1241.37	1179.68	1133.80	1098.76
294.15	1368.25	1288.80	1240.67	1178.99	1133.12	1098.10
295.15	1367.63	1288.10	1239.97	1178.30	1132.45	1097.43
296.15	1367.00	1287.41	1239.28	1177.62	1131.77	1096.77
297.15	1366.38	1286.71	1238.58	1176.93	1131.09	1096.31
298.15	1365.77	1286.02	1237.88	1176.24	1130.42	1095.65
299.15	1365.14	1285.33	1237.19	1175.55	1129.74	1094.99
300.15	1364.53	1284.64	1236.50	1174.87	1129.07	1094.32
301.15	1363.91	1283.95	1235.81	1174.19	1128.40	1093.65
302.15	1363.29	1283.26	1235.12	1173.50	1127.72	1092.99
303.15	1362.67	1282.57	1234.43	1172.82	1127.05	1092.32
304.15	1362.05	1281.89	1233.74	1172.14	1126.38	1091.66
305.15	1361.44	1281.20	1233.05	1171.46	1125.71	1090.99
306.15	1360.82	1280.52	1232.37	1170.78	1125.04	1090.33
307.15	1360.21	1279.84	1231.69	1170.11	1124.37	1089.66
308.15	1359.59	1279.15	1231.00	1169.43	1123.70	1089.00
309.15	1358.98	1278.48	1230.32	1168.75	1123.03	1088.33
310.15	1358.76	1277.80	1229.64	1168.08	1122.36	1087.67
311.15	1358.14	1277.12	1228.96	1167.41	1121.70	1087.00
312.15	1357.52	1276.44	1228.28	1166.73	1121.03	1086.34
313.15	1356.90	1275.76	1227.61	1166.06	1120.37	1085.68
314.15	1356.28	1275.09	1226.93	1165.39	1119.70	1085.02
315.15	1355.67	1274.41	1226.25	1164.73	1119.04	1084.36
316.15	1355.05	1273.74	1225.58	1164.06	1118.38	1083.70
317.15	1354.43	1273.07	1224.90	1163.39	1117.72	1083.04
318.15	1353.81	1272.40	1224.23	1162.73	1117.06	1082.38
319.15	1353.19	1271.72	1223.56	1162.06	1116.40	1081.72
320.15	1352.57	1271.05	1222.89	1161.40	1115.74	1081.06
321.15	1351.96	1270.38	1222.21	1160.74	1115.08	1080.40
322.15	1351.34	1269.71	1221.54	1160.07	1114.42	1079.75
323.15	1350.72	1269.04	1220.88	1159.41	1113.77	1079.09
324.15	1350.11	1268.37	1220.21	1158.76	1113.12	1078.44
325.15	1349.49	1267.71	1219.54	1158.10	1112.46	1077.78
326.15	1348.88	1267.04	1218.87	1157.43	1111.81	1077.13
327.15	1348.27	1266.38	1218.21	1156.78	1111.16	1076.48
328.15	1347.65	1265.71	1217.54	1156.12	1110.51	1075.83
329.15	1347.04	1265.05	1216.88	1155.47	1109.86	1075.17
330.15	1346.43	1264.39	1216.21	1154.81	1109.21	1074.52
331.15	1345.82	1263.72	1215.55	1154.16	1108.56	1073.87
332.15	1345.20	1263.06	1214.89	1153.51	1107.92	1073.23
333.15	1344.60	1262.40	1214.23	1152.85	1107.27	1072.58
334.15	1343.99	1261.74	1213.56	1152.20	1106.63	1071.93
335.15	1343.38	1261.08	1212.90	1151.55	1105.98	1071.29
336.15	1342.77	1260.42	1212.24	1150.90	1105.33	1070.64
337.15	1342.16	1259.76	1211.58	1150.25	1104.69	1070.00
338.15	1341.56	1259.10	1210.92	1149.60	1104.05	1069.35
339.15	1340.95	1258.44	1210.26	1148.95	1103.41	1068.71
340.15	1340.35	1257.78	1209.60	1148.30	1102.77	1068.07
341.15	1339.75	1257.13	1208.95	1147.65	1102.13	1067.43
342.15	1339.14	1256.47	1208.29	1147.01	1101.49	1066.79
343.15	1338.54	1255.81	1207.63	1146.37	1100.85	1066.15
344.15	1337.94	1255.15	1206.97	1145.72	1100.21	1065.51
345.15	1337.34	1254.50	1206.32	1145.07	1099.57	1064.87
346.15	1336.74	1253.84	1205.66	1144.43	1098.93	1064.23
347.15	1336.14	1253.19	1205.01	1143.78	1098.30	1063.60
348.15	1335.54	1252.54	1204.36	1143.14	1097.66	1062.96
349.15	1334.94	1251.88	1203.70	1142.50	1097.02	1062.32
350.15	1334.35	1251.23	1203.05	1141.85	1096.39	1061.69
351.15	1333.75	1250.58	1202.40	1141.21	1095.75	1061.05
352.15	1333.16	1249.93	1201.75	1140.57	1095.12	1060.42
353.15	1332.57	1249.28	1201.09	1139.93	1094.49	1059.79
354.15	1331.97	1248.63	1200.44	1139.29	1093.85	1059.16
355.15	1331.38	1247.98	1199.79	1138.65	1093.22	1058.53
356.15	1330.79	1247.33	1199.14	1138.01	1092.59	1057.89
357.15	1330.20	1246.68	1198.49	1137.37	1091.95	1057.26
358.15	1329.61	1246.03	1197.84	1136.73	1091.32	1056.63
359.15	1329.02	1245.38	1197.20	1136.09	1090.69	1056.00
360.15	1328.44	1244.74	1196.55	1135.45	1090.06	1055.37
361.15	1327.85	1244.09	1195.90	1134.82	1089.43	1054.75
362.15	1327.26	1243.44	1195.26	1134.18	1088.80	1054.12
363.15	1326.68	1242.80	1194.61	1133.54	1088.17	1053.49

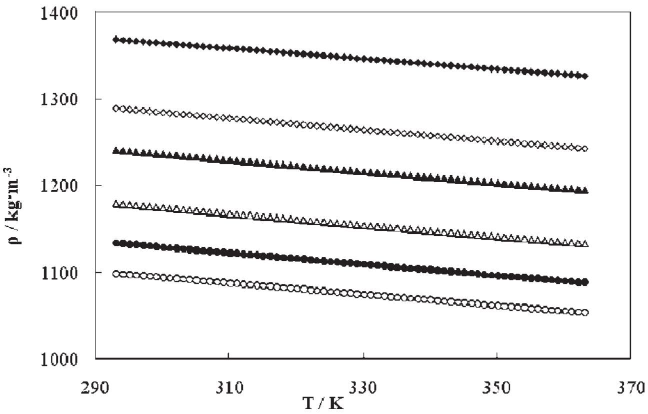


Figure 1. Experimental density data, ρ/kg·m^{-3}, of ILs with a common cation, 1-ethyl-3-methylimidazolium, $[C_2mim]^+$, and distinct alkyl sulfate and hydrogen sulfate anions, from (293.15 to 363.15) K at atmospheric pressure: ◆, $[HSO_4]^-$; ◇, $[C_1SO_4]^-$; ▲, $[C_2SO_4]^-$;[18] △, $[C_4SO_4]^-$; ●, $[C_6SO_4]^-$; ○, $[C_8SO_4]^-$.

α_p is 2 %. The temperature dependence of the isobaric expansion coefficient is very mild with a negative slope in the temperature range considered. This fact is not surprising as ILs present very modest T-dependences, and a minimum in the α_p versus T plots not far from room-temperature is usually found.[25] The α_p values increase with the alkyl chain length of the anion, displaying a similar behavior to that observed for the imidazolium cation[25] and the alkyl sulfonate anion.[12] The α_p values of comparable alkyl sulfates and alkyl sulfonates,[12] namely, methyl and ethyl side chains, are slightly higher for the former family. The α_p values for $[C_2mim][HSO_4]$ are much lower than those for the remaining

Table 4. Fitting Parameters for Density as a Function of Temperature Using the Quadratic Polynomial Equation (eq 1) for the Studied ILs with a Common Cation 1-Ethyl-3-methylimidazolium, $[C_2mim]^+$, and Distinct Alkyl Sulfate and Hydrogen Sulfate Anions[a]

	$A \pm \sigma_A$		$10^4 \cdot (B \pm \sigma_B)$		$10^7 \cdot (C \pm \sigma_C)$	
IL anion	$kg \cdot m^{-3}$		$kg \cdot m^{-3} \cdot K^{-1}$		$kg \cdot m^{-3} \cdot K^{-2}$	
$[HSO_4]^-$	7.34473	0.0022	−3.96840	0.137	−0.7790	0.209
$[C_1SO_4]^-$	7.33100	0.0004	−6.17220	0.022	1.3862	0.033
$[C_2SO_4]^-$	7.30017	0.0004	−6.44300	0.027	1.4716	0.041
$[C_4SO_4]^-$	7.25931	0.0005	−6.89350	0.029	1.8320	0.044
$[C_6SO_4]^-$	7.22467	0.0003	−7.06184	0.018	1.8245	0.027
$[C_8SO_4]^-$	7.18758	0.0015	−6.56240	0.095	0.8010	0.144

[a] All fittings have a correlation coefficient higher than 0.9999.

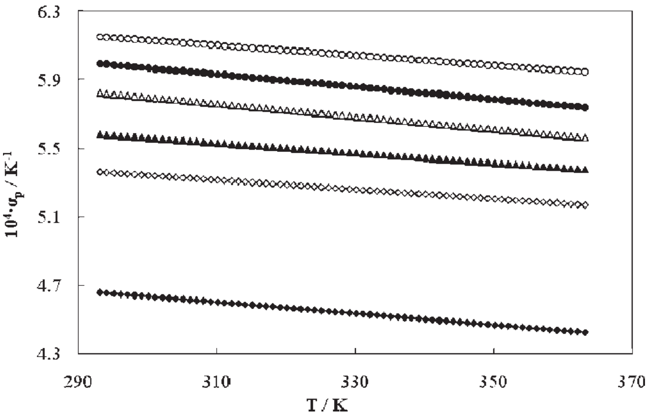


Figure 2. Isobaric thermal expansion coefficients, α_p/K^{-1}, of ILs with a common cation, 1-ethyl-3-methylimidazolium, $[C_2mim]^+$, and distinct alkyl sulfate and hydrogen sulfate anions, from (293.15 to 363.15) K at atmospheric pressure: ◆, $[HSO_4]^-$; ◇, $[C_1SO_4]^-$; ▲, $[C_2SO_4]^-$; △, $[C_4SO_4]^-$; ●, $[C_6SO_4]^-$; ○, $[C_8SO_4]^-$.

1-ethyl-3-methylimadazolium alkyl sulfate ILs, indicating that the $[HSO_4]^-$ anion cannot obviously be considered the first hypothetical member (C_0) of the alkyl sulfate family of anions. In conclusion, the isobaric thermal expansion coefficients for the ILs studied increase with the increase of the alkyl chain length of the anion, in other words: $[C_2mim][HSO_4] \ll [C_2mim][C_1SO_4] < [C_2mim][C_2SO_4] < [C_2mim][C_4SO_4] < [C_2mim][C_6SO_4] < [C_2mim][C_8SO_4]$.

Predictive Methods for Volumetric Properties. Although experimental data should always be the primary source of data, some methodologies based on group contribution methods are extremely useful in predicting the density, viscosity, and molar volume of ILs. Despite the highly complex liquid structure of ILs, their volumetric properties have been shown to behave very close to ideality. For instance, binary mixtures of two ILs present quasi-zero excess volumes.[26] This feature led to the establishment[27−29] of a very simple, albeit very precise, rule-of-thumb for predicting the molar volume of any aprotic IL. The volume is taken as the sum of the effective volumes occupied by the constituent cations and anions ($V_m = V^*_c + V^*_a$). The typical predictive power of this algorithm is better than 0.5 %. To establish a scale of effective volumes of cations and anions, we had to anchor the value of a reference ion. From calculations based on atomic radii, we established a value of 73.7 $cm^3 \cdot mol^{-1}$ for the effective volume occupied by $[PF_6]^-$ at 298.15 K.[29] Since the molar volume of the cation $[C_2mim]^+$ is well-defined in the literature,[27−29] measuring 99.20 $cm^3 \cdot mol^{-1}$ at 298.15 K and at atmospheric pressure, we used this methodology to predict the volumes of the distinct anions studied based on the Table 3 experimental density values. The volumes of the distinct anions appear in Table 5.

Table 5. Effective Molar Volume of the Alkyl Sulfate and Hydrogen Sulfate Anions at 298.15 K and Atmospheric Pressure Calculated in This Work Using an Effective Molar Volume of the Cation, $[C_2mim]^+$, of 99.20 $cm^3 \cdot mol^{-1}$ [27−29]

	V_m
IL anion	$cm^3 \cdot mol^{-1}$
$[HSO_4]^-$	53.27
$[C_1SO_4]^-$	73.63
$[C_2SO_4]^-$	91.68
$[C_4SO_4]^-$	125.53
$[C_6SO_4]^-$	159.46
$[C_8SO_4]^-$	193.27

The results show a CH_2 group increment of 17.21 $cm^3 \cdot mol^{-1}$ for the ILs with an alkyl chain length longer than methyl, which perfectly matches the range of values found in the literature for this group of 17.2 ± 0.3 $cm^3 \cdot mol^{-1}$; this universal increase occurs irrespective of the chemical nature and position (cation or anion) of the substituted alkyl side chain.[12,28] The results also reiterate that the C_0 alkyl side chain group, H, does not follow the former trend, presenting a molar volume addition of 20.36 $cm^3 \cdot mol^{-1}$ when changing from $[C_2mim][HSO_4]$ to $[C_2mim][C_1SO_4]$, as shown in Figure 3A.

Other methods are available to estimate the density of ILs, namely, the Ye and Shreeve method[21] and its extension proposed by Gardas and Coutinho,[20,24] which uses eq 3

$$\rho = \frac{M}{NV(a + bT + cP)} \tag{3}$$

in which ρ is the density in $kg \cdot m^{-3}$, M is the molar mass in $kg \cdot mol^{-1}$, N is the Avogadro constant, V is the molecular volume in Å^3, T is the temperature in K, and P is the pressure in MPa. The universal coefficients a, b, and c are 0.8005 ± 0.0002, $6.652 \cdot 10^{-4} \pm 0.007 \cdot 10^{-4}$ K^{-1}, and $-5.919 \cdot 10^{-4} \pm 0.024 \cdot 10^{-4}$ MPa^{-1}, respectively, at a 95 % confidence level.[20]

The group contributions for the molecular volumes of the studied ILs were taken from the literature[21,23] and are listed in Table 6. To compare the predicted values with our experimental data, we used the mean percent deviation (MPD) given by eq 4.

$$\mathrm{MPD}(\%) = \frac{100 \cdot \sum_i \left| \frac{(\rho_{\mathrm{cal}} - \rho_{\mathrm{exp}})}{\rho_{\mathrm{exp}}} \right|_i}{i} \tag{4}$$

The MPDs of the predicted density data were between 3.6 % and 7.1 %. Since these values are considered high for the estimation of density, we used our data to re-estimate the group contributions of the chemical groups present in each anion. The group contribution parameters of the cation are well-defined in the literature,[21] so only those of the anions were estimated. In

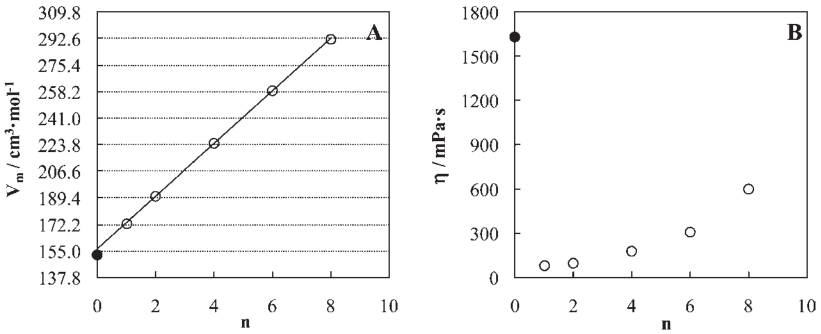


Figure 3. (A) Experimental molar volume, V_m/cm^3·mol^{-1}, and (B) experimental viscosity, η/mPa·s, of ILs with a common cation, 1-ethyl-3-methylimidazolium, [C_2mim]$^+$, and distinct alkyl sulfate (○) and hydrogen sulfate (●) anions, at 298.15 K and atmospheric pressure.

Table 6. Comparison between the Molecular Volume Contributions from the Literature and Those Calculated Using the Ye and Shreeve Method

species	V/m^3	
	literature[21,23]	calculated
	Cation	
1,3-dimethylimidazolium	$1.54 \cdot 10^{-28}$	-
	Anion	
$[SO_4]^{2-}$	$9.10 \cdot 10^{-29}$	-
$[HSO_4]^-$	$8.90 \cdot 10^{-29}$	$6.99 \cdot 10^{-29}$
$[C_1SO_4]^-$	-	$1.04 \cdot 10^{-28}$
	Groups	
CH_2	$2.80 \cdot 10^{-29}$	-
CH_2 in $[C_nSO_4]^-$ with $n > 1$	-	$2.88 \cdot 10^{-29}$
CH_3	$3.50 \cdot 10^{-29}$	-

Table 7. Experimental Viscosity Data, η/mPa·s, of ILs with a Common Cation 1-Ethyl-3-methylimidazolium, [C_2mim]$^+$, and Distinct Alkyl Sulfate and Hydrogen Sulfate Anions, from (283.15 to 373.15) K at Atmospheric Pressure

	$[HSO_4]^-$	$[C_1SO_4]^-$	$[C_4SO_4]^-$	$[C_6SO_4]^-$	$[C_8SO_4]^-$
T/K	η/mPa·s	η/mPa·s	η/mPa·s	η/mPa·s	η/mPa·s
283.15	5756.7	169.5	468.4	875.0	1879.0
288.15	3635.0	128.6	332.5	604.0	1252.1
293.15	2389.9	99.7	242.3	428.3	856.0
298.15	1628.4	78.8	180.8	311.4	601.6
303.15	1144.8	63.4	137.9	231.5	433.6
308.15	827.1	51.8	107.2	175.7	319.6
313.15	612.2	42.9	84.8	135.9	240.5
318.15	463.0	35.9	68.1	106.9	184.4
323.15	356.8	30.5	55.6	85.4	143.8
328.15	279.7	26.1	45.9	69.2	113.9
333.15	222.6	22.6	38.4	56.8	91.6
338.15	179.6	19.7	32.4	47.2	74.5
343.15	146.7	17.3	27.7	39.6	61.4
348.15	121.2	15.3	23.8	33.6	51.1
353.15	101.2	13.6	20.7	28.8	43.0
358.15	85.2	12.2	18.1	24.8	36.5
363.15	72.4	11.0	16.0	21.6	31.3
368.15	61.9	9.9	14.2	18.9	27.0
373.15	53.4	9.0	12.6	16.7	23.5

calculating the new group contribution parameters, the MPD as defined in eq 4 was minimized. The results show the same type of behavior as the previous method: the hydrogen sulfate anion does not belong to the alkyl sulfate anion series. From the experimental density data, the molecular volume of the $[HSO_4]^-$, $[C_1SO_4]^-$, and CH_2 groups in the alkyl sulfate anion with $n > 1$ were calculated and appear in Table 6. The CH_2 group in the alkyl sulfate anion with the $n > 1$ contribution was obtained through the weighted average of the CH_2 group contribution for the alkyl sulfates for $n > 1$. The MPD from the new group contributions is smaller than 0.8 %.

Viscosities. The viscosity data for the [C_2mim][$C_n$$SO_4$] family appear as a function of temperature in Table 7 and are illustrated in Figure 4. Only one paper[15] presents viscosity data for the ILs used in this work. Himmler et al. studied the ILs [C_2mim][C_4SO_4], [C_2mim][C_6SO_4], and [C_2mim][C_8SO_4] and reported data only at 293.15 K. There is a significant difference between the data sets, with our results showing higher values. The deviations are 13 % for [C_2mim][C_4SO_4] and [C_2mim][C_6SO_4] and 24 % for [C_2mim][C_8SO_4]. Himmler et al. mention that their samples contained around 600 ppm of water. Even small amounts of water are known to significantly decrease the viscosity of ILs, so this is the likely explanation.

Although the IL structure has a visible effect on viscosity, especially in the lower temperature range, the strongest effect on viscosity comes from temperature. The experimental data identified the following viscosity order: [C_2mim][C_1SO_4] < [C_2mim][C_2SO_4] < [C_2mim][C_4SO_4] < [C_2mim][C_6SO_4] < [C_2mim][C_8SO_4] < [C_2mim][HSO_4]. The high viscosity for [C_2mim][HSO_4], explicitly observed in Figure 3B, can be explained by the larger Coulombic interactions of the hydrogen sulfate anion compared with the rest of the alkyl sulfate anion series. In the hydrogen sulfate anion, the absence of any alkyl chain allows for a stronger cation/anion interaction and, consequently, more efficient packing. This is also reflected by the higher density of [C_2mim][HSO_4] as compared to that estimated by the extrapolation of the density values to $C_{n=0}$ using the alkyl sulfate family. We can state that the viscosity increases as the alkyl side chain in the anion grows, from the [C_2mim][C_1SO_4] onward, due to the rise in the van der Waals interactions as the alkyl side chain lengthens.[30] This can also be explained by the enlargement of the apolar nanosegregated domain proposed in the literature for the larger members of this family.[31]

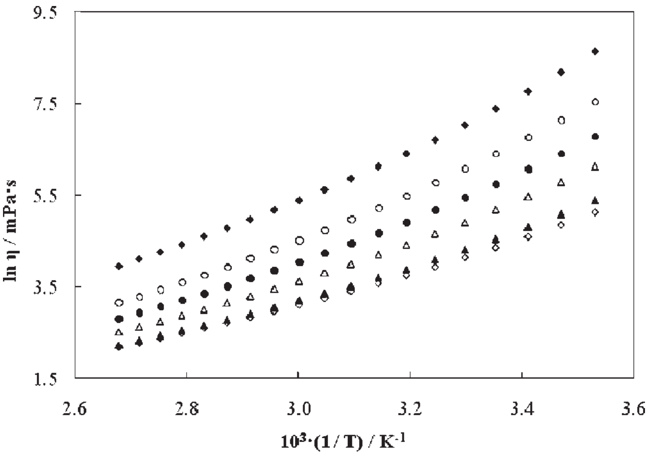


Figure 4. Experimental viscosity data, $\ln(\eta/\mathrm{mPa \cdot s})$, of ILs with a common cation, 1-ethyl-3-methylimidazolium, $[C_2mim]^+$, and distinct alkyl sulfate and hydrogen sulfate anions, from (283.15 to 373.15) K at atmospheric pressure: ◆, $[HSO_4]^-$; ◇, $[C_1SO_4]^-$; ▲, $[C_2SO_4]^-$;[19] △, $[C_4SO_4]^-$; ●, $[C_6SO_4]^-$; ○, $[C_8SO_4]^-$.

Table 8. Comparison between the IL Group Contributions to the *A* and *B* Parameters Given in Literature and Those Calculated Using the Orrick–Erbar-Type Approach

species	literature[22]		calculated	
	A	*B*/K	*A*	*B*/K
	Cation			
1,3-dimethylimidazolium	6.56	1757.1	-	-
	Anion			
$[HSO_4]^-$	-	-	−21.76	3198.4
$[C_1SO_4]^-$	−19.46	1732.8	−18.25	1266.1
	Groups			
CH_2	−0.63	250.4	-	-
CH_2 in $[C_nSO_4]^-$ with $n > 1$	-	-	−0.54	237.0
CH_3	−0.74	250.0	-	-

The literature data for the alkyl sulfonate-based ILs only display the effect of increasing the alkyl chain length in the anion from $[C_2mim][C_1SO_3]$ to $[C_2mim][C_4SO_3]$. Comparing the alkyl sulfate-based ILs with the similar alkyl sulfonate family, a similar increase in viscosity occurs with the lengthening of the alkyl side chain in both IL families. However, alkyl sulfate-based ILs are less viscous (2 to 3 times so at low temperatures) than the corresponding alkyl sulfonates,[12] which is an industrial advantage. The difference between these two similar families relates to their structures, specifically the extra oxygen bridge atom in the sulfate anion.[32] This oxygen atom in the sulfate anion contributes to a large polar character, decreasing the van der Waals interactions, and decreasing viscosity.

Predictive Methods for Viscosity. Several methods are available in the literature for predicting IL viscosity. We used two: the Orrick–Erbar and the Vogel–Fulcher–Tammann. The former states that the temperature dependence of viscosity is that given by eq 5

$$\ln\left(\frac{\eta}{\rho M}\right) = A + \frac{B}{T} \tag{5}$$

Table 9. Comparison between the Group Contributions to the Parameters $a_{i,\eta}$ and $b_{i,\eta}$ Given in Literature and Those Calculated Using the Vogel–Tammann–Fulcher Method

species	literature[24]		calculated	
	$a_{i,\eta}$	$b_{i,\eta}$/K	$a_{i,\eta}$	$b_{i,\eta}$/K
	Cation			
1,3-dimethylimidazolium	−7.271	510.51	-	-
	Anion			
$[HSO_4]^-$	-	-	−1.650	707.35
$[C_1SO_4]^-$	−1.580	339.90	−1.204	248.39
$[C_2SO_4]^-$	−1.499	317.87	−1.444	303.86
$[C_4SO_4]^-$	-	-	−1.772	432.44
$[C_6SO_4]^-$	-	-	−1.966	532.22
$[C_8SO_4]^-$	-	-	−2.184	649.02
	Groups			
CH_2	−0.075	40.92	-	-
CH_3	−0.002	8.02	-	-

where η is the viscosity in mPa·s, ρ is the density in $g \cdot cm^{-3}$, M is the molecular weight in $g \cdot mol^{-1}$, and T is the absolute temperature in K. A and B are parameters that can be estimated using group contribution methods. In the literature[22] group contributions are already available for the cation $[C_1mim]^+$ and the CH_2 contribution and for the anions $[C_1SO_4]^-$ and $[C_2SO_4]^-$. It is important to point out that the CH_2 additive group in the literature has only been derived for the cation. However, by analyzing the CH_2 contribution when changing from $[C_1SO_4]^-$ to $[C_2SO_4]^-$ we can see that the signal is opposite. Table 8 presents all of the groups from the literature for the ILs under consideration.

Direct analysis using the available groups for $[C_2mim][C_1SO_4]$ and $[C_2mim][C_2SO_4]$ showed that the predicted viscosity had an MPD of 6.3 % for the former IL and 8.6 % for the latter. Considering that the CH_2 group contribution also applies to the anion, we predicted the viscosity for the other ILs. MPDs of 15 % for $[C_2mim][C_4SO_4]$ up to 90 % for $[C_2mim][HSO_4]$ were obtained. Thus, on the basis of these high deviations, it is important to use our data to recalculate the group contributions for the anions of the alkyl sulfate family.

As, once again, the contribution of the cation is well-defined in the literature, we calculated the contribution of chemical groups present in the anion for the A and B parameters using our experimental viscosity data. They showed that the $[HSO_4]^-$ anion does not belong to the alkyl sulfate series. Table 8 presents the A and B parameters for $[HSO_4]^-$ and $[C_1SO_4]^-$ with the latter acting as an anchor for the rest of the family. The CH_2 group contribution was calculated using the weighted average of the contributions obtained for all ILs analyzed, with the exception of $[C_2mim][HSO_4]$. With this contribution in the anion, we predicted the viscosity values according to the Orrick–Erbar method for $[C_2mim][C_nSO_4]$ with $n > 1$ giving an MPD between (3.4 and 9.6) % depending on the IL. According to eq 5, the Orrick–Erbar approach needs density data. To overcome this methodological limitation, we tested the Vogel–Tammann–Fulcher correlation represented by eq 6.

$$\ln \eta = A_\eta + \frac{B_\eta}{(T - T_{0\eta})} \tag{6}$$

The viscosity in Pa·s is represented by η, T is the temperature in K, and A_η, B_η, and $T_{0\eta}$ are adjustable parameters. The A_η and B_η parameters are obtained using a group contribution method based on eq 7.

$$A_\eta = \sum_{i=1}^{k} n_i a_{i,\eta} \quad \text{and} \quad B_\eta = \sum_{i=1}^{k} n_i b_{i,\eta} \tag{7}$$

According to the literature,[24] the optimal value of $T_{0\eta}$ for the application of this correlation to ILs is 165.06 K. The parameters available appear in Table 9. The methodology previously used was repeated here, and the predicted viscosity values for $[C_1SO_4]^-$ and $[C_2SO_4]^-$ have MPDs of 4.7 % and 3.4 %, respectively. For the other members of the *n*-alkyl sulfate family, the largest deviation in predicted viscosity occurred for $[C_2mim][HSO_4]$ with an MPD of about 90 %. For longer alkyl chains, the deviations dropped to values of 6.3 up to 16.6 %.

As pointed out previously, since large errors were obtained in the prediction of viscosity, new parameters for the anions were calculated and appear in Table 9. The results show that, in this method, the CH_2 group contribution is not additive. To overcome this problem, Table 9 shows the values for all anions. The fitting of these new group contribution parameters gives an MPD between 0.1 % and 0.6 %.

CONCLUSIONS

Density and viscosity data of 1-ethyl-3-methylimidazolium-based ILs, with alkyl sulfate (n = 1, 4, 6, and 8) and hydrogen sulfate anions from 283.15 K up to 373.15 K were obtained. As expected, the results clearly show that the IL $[C_2mim][HSO_4]$ does not belong to the alkyl sulfate family and that an increase of the alkyl chain length of the alkyl sulfate anion decreases density and increases viscosity.

Thermal expansion coefficients were calculated from the density data. A second-order polynomial equation was used to fit the density data, implying a dependence of the thermal expansion coefficient with temperature. As for most ILs, this property decreases with increasing temperature in this temperature range.

The experimental density results confirm the increment of 17.21 $cm^3 \cdot mol^{-1}$ in molar volume per CH_2 group added to the alkyl chain of the anion proposed in the literature for the imidazolium cation.

Group contribution methods, namely, Ye–Schreeve for density and Orrick–Erbar and Vogel–Tammann–Fulcher for viscosity, were used to predict both properties. Since the predicted density and viscosity values based on the existing parameters show large deviations from the experimental data, new contribution group parameters for each method were proposed for the alkyl sulfate anions.

AUTHOR INFORMATION

Corresponding Author

*E-mail: imarrucho@itqb.unl.pt; jmesp@itqb.unl.pt.

Funding Sources

The work was partially supported by a grant from Iceland, Liechtenstein, and Norway through the EEA financial mechanism (Project PT015). Financial support was also provided by *Fundação para a Ciência e Tecnologia* (FCT) through projects PTDC/CTM/73850/2006, PTDC/QUI/71331/2006, and PTDC/QUI/72903/2006. J.M.S.S.E. and I.M.M. acknowledge FCT for a contract from *Programa Ciência* 2007. The National NMR Network (REDE/1517/RMN/2005), was supported by POCI 2010 and Fundação para a Ciência e a Tecnologia.

REFERENCES

(1) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Filipe, E. On the critical temperature, normal boiling point and vapour pressure of ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 6040–6043.

(2) Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831–834.

(3) Esperança, J. M. S. S.; Canongia Lopes, J. N.; Tariq, M.; Santos, L. M. N. B. F.; Magee, J. W.; Rebelo, L. P. N. Volatility of Aprotic Ionic Liquids - A Review. *J. Chem. Eng. Data* **2010**, *55*, 3–12.

(4) Smiglak, M.; Reichert, W. M.; Holbrey, J. D.; Wilkes, J. S.; Sun, L. Y.; Thrasher, J. S.; Kirichenko, K.; Singh, S.; Katritzky, A. R.; Rogers, R. D. Combustible ionic liquids by design: Is laboratory safety another ionic liquid myth?. *Chem. Commun.* **2006**, 2554–2556.

(5) Azevedo, R. G.; Esperança, J. M. S. S.; Szydlowski, J.; Visak, Z. P.; Pires, P. F.; Guedes, H. J. R.; Rebelo, L. P. N. Thermophysical and Thermodynamic Properties of Ionic Liquids over an Extended Pressure Range: $[bmim][NTf_2]$ and $[hmim][NTf_2]$. *J. Chem. Thermodyn.* **2005**, *37*, 888–899.

(6) Azevedo, R. G.; Esperança, J. M. S. S.; Najdanovic-Visak, V.; Visak, Z. P.; Guedes, H. J. R.; Nunes da Ponte, M.; Rebelo, L. P. N. Thermophysical and Thermodynamic Properties of 1-Butyl-3-methylimidazolium Tetrafluoroborate and 1-Butyl-3-methylimidazolium Hexafluorophosphate over an Extended Pressure Range. *J. Chem. Eng. Data* **2005**, *50*, 997–1008.

(7) Esperança, J. M. S. S.; Guedes, H. J. R.; Canongia Lopes, J. N.; Rebelo, L. P. N. Pressure-density-temperature (p-ρ-T) surface of $[C_6mim][NTf_2]$. *J. Chem. Eng. Data* **2008**, *53*, 867–870.

(8) Tariq, M.; Carvalho, P. J.; Coutinho, J. A. P.; Marrucho, I. M.; Lopes, J. N. C.; Rebelo, L. P. N. Viscosity of (C2–C14) 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids in an extended temperature range. *Fluid Phase Equilib.* **2011**, *301*, 22–32.

(9) Paulechka, Y. U. Heat Capacity of Room-Temperature Ionic Liquids: A Critical Review. *J. Phys. Chem. Ref. Data* **2010**, *39*, 033108 (23 pages).

(10) Marsh, K.; Boxall, J.; Lichtenthaler, R. Room temperature ionic liquids and their mixtures – a review. *Fluid Phase Equilib.* **2004**, *219*, 93–98.

(11) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

(12) Blesic, M.; Swadzba-Kwasny, M.; Belhocine, T.; Gunaratne, H. Q. N.; Lopes, J. N. C.; Gomes, M. F. C.; Pádua, A. A. H.; Seddon, K. R.; Rebelo, L. P. N. 1-Alkyl-3-methylimidazolium alkanesulfonate ionic liquids, $[C_nH_{2n+1}mim][C_kH_{2k+1}SO_3]$: synthesis and physicochemical properties. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8939–8948.

(13) Blesic, M.; Swadzba-Kwasny, M.; Belhocine, T.; Holbrey, J.; Lopes, J.; Gomes, M.; Pádua, A.; Seddon, K.; Rebelo, L. New catanionic surfactants based on 1-alkyl-3-methylimidazolium alkylsulfonates, $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$: mesomorphism and aggregation. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4260–4268.

(14) Russina, O.; Gontrani, L.; Fazio, B.; Lombardo, D.; Triolo, A.; Caminiti, R. Selected chemical–physical properties and structural heterogeneities in 1-ethyl-3-methylimidazolium alkyl-sulfate room temperature ionic liquids. *Chem. Phys. Lett.* **2010**, *493*, 259–262.

(15) Himmler, S.; Hormann, S.; van Hal, R.; Schulza, P. S.; Wasserscheid, P. Transesterification of methylsulfate and ethylsulfate ionic liquids - an environmentally benign way to synthesize long-chain and functionalized alkylsulfate ionic liquids. *Green Chem.* **2006**, *8*, 887–894.

(16) Shekaari, H.; Armanfar, E. Apparent molar volumes and expansivities of aqueous solutions of ionic liquids, 1-alkyl-3-methylimidazolium alkyl sulfate at T = (298.15−328.15) K. *Fluid Phase Equilib.* **2011**, *303*, 120–125.

(17) Ficke, L. E.; Novak, R. R.; Brennecke, J. F. Thermodynamic and Thermophysical Properties of Ionic Liquid + Water Systems. *J. Chem. Eng. Data* **2010**, *55*, 4946–4950.

(18) Castro, C. A. N.; Langa, E.; Morais, A. L.; Lopes, M. L. M.; Lourenço, M. J. V.; Santos, F. J. V.; Santos, M. S. C. S.; Lopes, J. N. C.; Veiga, H. I. M.; Macatrão, M.; Esperança, J. M. S. S.; Marques, C. S.; Rebelo, L. P. N.; Afonso, C. A. M. Studies on the density, heat capacity, surface tension and infinite dilution diffusion qith the ionic liquids [C_4mim][NTf_2], [C_4mim][dca], [C_2mim][$EtOSO_3$] and [Aliquat][dca]. *Fluid Phase Equilib.* **2010**, *294*, 157–179.

(19) Tariq, M., et al. Unpublished results, personal communication; ITQB/UNL, 2011.

(20) Gardas, R. L.; Coutinho, J. A. P. Extension of the Ye and Shreeve group contribution method for density estimation of ionic liquids in a wide range of temperatures and pressures. *Fluid Phase Equilib.* **2008**, *263*, 26–32.

(21) Ye, C.; Shreeve, J. M. Rapid and accurate estimation of densities of room-temperature ionic liquids and salts. *J. Phys. Chem. A* **2007**, *111*, 1456–1461.

(22) Gardas, R. L.; Coutinho, J. A. P. A group contribution method for viscosity estimation of ionic liquids. *Fluid Phase Equilib.* **2008**, *266*, 195–201.

(23) Jenkins, H. D. B.; Roobottom, H. K. Relationships among ionic lattice energies, molecular (formula unit) volumes, and thermochemical radii. *Inorg. Chem.* **1999**, *38*, 3609–3620.

(24) Gardas, R. L.; Coutinho, J. A. P. Group contribution methods for the prediction of thermophysical and transport properties of ionic liquids. *AIChE J.* **2009**, *55*, 1274–1287.

(25) Tariq, M.; Serro, A. P.; Mata, J. L.; Saramago, B.; Esperança, J. M. S. S.; Canongia Lopes, J. N.; Rebelo, L. P. N. High-temperature surface tension and density measurements of 1-alkyl-3-methylimidazolium bistriflamide ionic liquids. *Fluid Phase Equilib.* **2010**, *294*, 157–179.

(26) Guedes, H. J. R.; Cordeiro, T. C.; Lopes, J. N. C.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Huq, S.; Seddon, K. R. Deviations from ideality in mixtures of two ionic liquids containing a common ion. *J. Phys. Chem. B* **2005**, *109*, 3519–3525.

(27) Esperança, J. M. S. S.; Guedes, H. J. R.; Blesic, M.; Rebelo, L. P. N. Densities and Derived Thermodynamic Properties of Ionic Liquids. 3. Phosphonium-Based Ionic Liquids over an Extended Pressure Range. *J. Chem. Eng. Data* **2006**, *51*, 237–242.

(28) Rebelo, L. P. N.; Lopes, J. N. C.; Esperança, J. M. S. S.; Guedes, H. J. R.; Lachwa, J.; Najdanovic−Visak, V.; Visak, Z. P. Accounting for the Unique, Doubly Dual Nature of Ionic Liquids from a Molecular Thermodynamic and Modeling Standpoint. *Acc. Chem. Res.* **2007**, *40*, 1114–1121.

(29) Rebelo, L. P. N.; Najdanovic-Visak, V.; Gomes de Azevedo, R.; Esperança, J. M. S. S.; Nunes da Ponte, M.; Guedes, H. J. R.; Visak, Z. P.; de Sousa, H. C.; Szydlowski, J.; Canongia Lopes, J. N.; Cordeiro, T. C. Phase Behavior and Thermodynamic Properties of Ionic Liquids, Ionic Liquid Mixtures, and Ionic Liquid Solutions. In *Ionic Liquids, IIIA: Fundamentals, Progress, Challenges, and Opportunities-Properties and Structure*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington DC, 2005; pp 270−291.

(30) Santos, L. M. N. B. F.; Canongia Lopes, J. N.; Coutinho, J. A. P.; Esperança, J. M. S. S.; Gomes, L. R.; Marrucho, I. M.; Rebelo, L. P. N. Ionic Liquids: First Direct Determination of their Cohesive Energy. *J. Am. Chem. Soc.* **2007**, *129*, 284–285.

(31) Canongia Lopes, J. N. A. C.; Padua, A. A. H. Nanostructural Organization in Ionic Liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.

(32) Deive, F. J.; Rodriguez, A.; Pereiro, A. B.; Shimizu, K.; Forte, P. A. S.; Romão, C. C.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Rebelo, L. P. N. Phase equilibria of haloalkanes dissolved in ethylsulfate- or ethylsulfonate-based ionic liquids. *J. Phys. Chem. B* **2010**, *114*, 7329–7337.