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Thermophysical Characterization of Ionic Liquids Able To Dissolve Biomass

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S *Supporting Information*

ABSTRACT: Among new potential solvents for lignocellulosic materials, ionic liquids (ILs) are attracting considerable attention. Hence, the knowledge of the thermophysical properties of such fluids is essential for the design of related industrial processes. Therefore, in this work, a set of thermophysical properties, namely, density, viscosity, and refractive index, as a function of temperature, and isobaric thermal expansivity and heat capacities at a constant temperature, were determined for eight ionic liquids with the 1-ethyl-3-methylimidazolium cation combined with the following anions: acetate, methylphosphonate, methanesulfonate, trifluoromethanesulfonate, dicyanamide, thiocyanate, tosylate, and dimethylphosphate. Imidazolium-based ILs were chosen since these are the most studied ionic fluids in biomass dissolution approaches, while a large array of anions was investigated because it was already demonstrated that it is the IL anion that mainly governs the dissolution.

INTRODUCTION

Wood is composed of cellulose, (35 to 50) %, lignin, (18 to 30) %, hemicelluloses, (15 to 30) %, and small amounts of extractive compounds.[1] Because of the complex composition and structure of lignocellulosic materials, their fractionation, in an effective and rentable way, is still a challenge target. Industrially, wood fractionation into cellulosic pulp and lignin is predominantly attained by the kraft process, which is not comprehensive in the utilization of noncellulosic components and causes complaints from the standpoint of environmental concerns.[2] In this context, ionic liquids (ILs) have been recently explored as novel solvents for lignocellulosic materials.[3−5] ILs are liquid salts (by common definition with melting temperatures below 100 °C) constituted by large and asymmetric organic cations and organic or inorganic anions. Due to the ions' large size and their conformational flexibility, ILs present low lattice enthalpies and large entropy changes upon melting which favor the liquid state. In general, ILs present a large liquid temperature range, high thermal and chemical stabilities, high ionic conductivities, and negligible vapor pressures, which further allow the fluid recycling in many processes. One of the main and additional attributes of ILs falls on their enhanced ability to dissolve the most diverse compounds.[6−8]

A pioneer work by Rogers and co-workers[9] has shown that hydrophilic ILs can efficiently dissolve cellulose. In the same line of research, later on, it was demonstrated that the solubility of cellulose increases almost linearly with the increase on the hydrogen bond accepting ability of the anions composing the ILs.[10] IL anions that can strongly coordinate with the hydrogen bond donor groups of cellulose are able to trigger solute−solvent interactions that are required to an improved dissolution.[11] As a result, the control of the dissolution of cellulose in ILs has provided a new platform for the polymer processing.[12,13]

Subsequently, it was found that not only cellulose could be dissolved in ILs, but also wood can be dissolved in the same fluids after mild grinding and that biomass could be selectively separated into its components with relative efficiency.[14−16] Recent reports[17,18] have additionally shown that ILs are also able to extract different polysaccharides from wood and others forms of lignocellulosic biomass. ILs have further been applied for the pretreatment and conversion of lignocellulosic materials.[19] In addition, it was established that biomaterials treated in IL media had a higher rate of enzymatic hydrolysis and yield of reducing sugars than those treated by traditional pretreatment methods.[20,21] In the past few years, acid-catalyzed dehydration of saccharides into furanic compounds making use of ILs has also received significant attention.[22,23]

In summary, the IL ability for biomass processing depends largely on the hydrogen-bond accepting ability of the anions that composed them. Due to their relative novelty and to the large array of possible ILs, most of them still have their thermophysical properties poorly characterized, and a complete database is far from being accomplished. In the current work, the thermophysical properties of eight ILs, namely, the density, viscosity, and refractive index, in broad temperature ranges, as well as isobaric thermal expansivity and heat capacities, at a constant temperature, were measured and presented. Since it was previously shown that the IL anion plays a crucial role toward the pretreatment and processing of biomass, the ILs studied here share the cation 1-ethyl-3-methylimidazolium while being combined with

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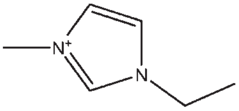
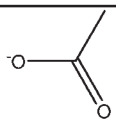
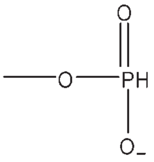
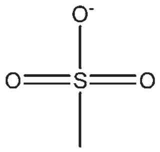
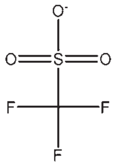
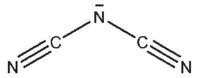
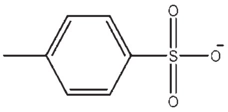
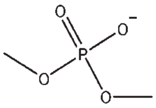
Table 1. Chemical Structures of the Ionic Liquids Studied

Ionic Species	Abbreviation	Ionic Structure
	Cation	
1-ethyl-3-methylimidazolium	$[C_2mim]^+$	
	Anion	
Acetate	$[CH_3CO_2]^-$	
Methylphosphonate	$[CH_3OHPO_2]^-$	
Methanesulfonate	$[CH_3SO_3]^-$	
Trifluoromethanesulfonate	$[CF_3SO_3]^-$	
Dicyanamide	$[N(CN)_2]^-$	
Thiocyanate	$[SCN]^-$	
Tosylate	$[Tos]^-$	
Dimethylphosphate	$[(OCH_3)_2PO_2]^-$	

a variety of different anions. The effect of the IL anion upon the measured properties is presented and discussed.

■ EXPERIMENTAL SECTION

Materials. Eight ionic liquids were studied in this work: 1-ethyl-3-methylimidazolium acetate, [C$_2$mim][CH$_3$CO$_2$], 1-ethyl-3-methylimidazolium methylphosphonate, [C$_2$mim][CH$_3$OHPO$_2$], 1-ethyl-3-methylimidazolium methanesulfonate, [C$_2$mim][CH$_3$SO$_3$], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (triflate), [C$_2$mim][CF$_3$SO$_3$], 1-ethyl-3-methylimidazolium dicyanamide, [C$_2$mim][N(CN)$_2$], 1-ethyl-3-methylimidazolium thiocyanate, [C$_2$mim][SCN], 1-ethyl-3-methylimidazolium tosylate, [C$_2$mim][Tos], and 1-ethyl-3-methylimidazolium dimethylphosphate, [C$_2$mim][(OCH$_3$)$_2$PO$_2$]. All ILs were acquired at Iolitec, with the exception of 1-ethyl-3-methylimidazolium methylphosphonate, which was purchased from Solvionic. The chemical structures of all investigated ILs are presented in Table 1.

To remove water and volatile impurities, IL samples were dried by heating ($\approx$ 343 K), with constant stirring, and at high vacuum ($\approx 10^{-4}$ Pa) for a minimum time period of 48 h. After this procedure, the purity of all IL samples was checked by ^{1}H and ^{13}C (and ^{19}F NMR for [C$_2$mim][CF$_3$SO$_3$]) NMR, where it was shown to be $\geq$ 0.99 mass fraction. Before the determination of the thermophysical properties of ILs, their water mass fraction content was determined by Karl Fischer titration, using a Metrohm 831 Karl Fischer coulometer. The reagent used was Hydranal Coulomat AG from Riedel-de Haën. After the measurements on the IL thermophysical properties, the water mass content was further determined to ascertain the water uptake of ILs during the experimental procedures. No significant differences were observed. The average water content in each IL is reported in Table 2.

Experimental Procedure. *Density and Viscosity.* Measurements of density, ρ, and dynamic viscosity, η, were performed using an automated SVM 3000 Anton Paar rotational Stabinger viscometer—densimeter. Density and viscosity measurements were carried out in the temperature range from (278.15 to 363.15) K and at $p \approx 0.1$ MPa. Since the ILs $[C_2mim][Tos]$ and $[C_2mim][(OCH_3)_2PO_2]$ are solid at room temperature, densities and viscosities for these ILs were only determined above their melting temperatures. The SVM 3000 Anton Paar rotational Stabinger viscometer—densimeter uses Peltier elements for fast and efficient thermostatization. Further details regarding the operational system can be found elsewhere.[24] The uncertainty in temperature is within ± 0.02 K. The relative uncertainty in the dynamic viscosity is ± 0.35 %, and the absolute uncertainty in density is $\pm (5 \cdot 10^{-4})\ g \cdot cm^{-3}$. The viscometer-densimeter equipment used in this work for the determination of density and viscosity of ILs was validated in previous works published by our group.[24−26]

Table 2. Average Water Content (Before and After the Experimental Measurements) for the Studied Ionic Liquids

ionic liquid	water content/(wt %)
$[C_2mim][CH_3CO_2]$	0.124
$[C_2mim][CH_3OHPO_2]$	0.078
$[C_2mim][CH_3SO_3]$	0.029
$[C_2mim][CF_3SO_3]$	0.002
$[C_2mim][N(CN)_2]$	0.006
$[C_2mim][SCN]$	0.027
$[C_2mim][Tos]$	0.056
$[C_2mim][(OCH_3)_2PO_2]$	0.014

Heat Capacity. The heat capacities of the studied ILs were measured at $T = 298.15$ K, using a high-precision heat capacity drop calorimeter, which is described in detail in the literature.[27−29] The calorimeter was calibrated with water and sapphire (α-Al_2O_3 pellets, NIST-RM 720) based on a $\Delta T = 10$ K drop procedure, using the respective standard molar heat capacities at 298.15 K reported in literature, $C^{\circ}_{p,m}$ (α-aluminum oxide) = $(79.03 \pm 0.08)\ J \cdot K^{-1} \cdot mol^{-1}$ and $C^{\circ}_{p,m}(H_2O) = (75.32 \pm 0.01)\ J \cdot K^{-1} \cdot mol^{-1}$.[30] The calibration constant was found to be $\varepsilon = (6.6329 \pm 0.0046)\ W \cdot V^{-1}$. The accuracy of the apparatus for the measurements of the heat capacities of liquids and solids was evaluated before, based on the measurements of benzoic acid and hexafluorobenzene.[28] Since the calorimeter was used to measure the heat capacity of ILs, its accuracy was additionally checked based on the results obtained for 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6mim][NTf_2]$.[31] The determined $C^{\circ}_{p,m}$ ($[C_6mim][NTf_2]$, 298.15 K) = $(629.46 \pm 1.63)\ J \cdot K^{-1} \cdot mol^{-1}$ is in excellent agreement with the available literature data ($C^{\circ}_{p,m}$ ($[C_6mim][NTf_2]$, 298.15 K) = $(631.6 \pm 0.5)\ J \cdot K^{-1} \cdot mol^{-1}$).[31−33] The IL $[C_2mim][(OCH_3)_2PO_2]$ is solid at room temperature, and its heat capacity at 298.15 K refers to the subcooled liquid.

Refractive Index. The refractive indices were measured at the sodium D-line using a Bellingham model RFM340 refractometer ($\pm 3 \cdot 10^{-5}$ stated precision), as a function of temperature, with temperatures above the respective ionic liquid melting points. The apparatus was calibrated by measuring the refractive index of degassed water (Millipore quality) and toluene. The temperature in the refractometer cell was controlled using an external thermostatic bath and measured by a 1/10 class Pt100 RTD in a Keithley data acquisition system 2700/7700 DMM/MUX and in a four-wire mode. The Pt100 temperature probe was previously calibrated against a calibrated platinum resistance thermometer, SPRT100 (Fluke-Hart Scientific 1529 Chub-E4), traceable to the National Institute of Standards and Technology (NIST), with an

Table 3. Experimental Density Values, ρ, for the Studied Ionic Liquids as a Function of Temperature and at 0.1 MPa

T	$\rho/(kg \cdot m^{-3})$							
K	$[C_2mim]$ $[CH_3CO_2]$	$[C_2mim]$ $[CH_3OHPO_2]$	$[C_2mim]$ $[CH_3SO_3]$	$[C_2mim]$ $[CF_3SO_3]$	$[C_2mim]$ $[N(CN)_2]$	$[C_2mim]$ $[SCN]$	$[C_2mim]$ $[Tos]$	$[C_2mim]$ $[(OCH_3)_2PO_2]$
278.15	1112.4	1222.2	1257.1	1403.3	1117.9	1129.7		
283.15	1108.9	1218.6	1253.3	1398.9	1114.3	1126.5		
288.15	1105.6	1215.1	1249.5	1394.5	1110.9	1123.3		
293.15	1102.4	1211.7	1245.9	1390.2	1107.4	1120.1		
298.15	1099.3	1208.3	1242.4	1385.9	1104.0	1117.0		
303.15	1096.2	1205.0	1239.0	1381.6	1100.6	1113.9	1223.4	1213.9
308.15	1093.6	1201.8	1235.6	1377.3	1097.3	1110.8	1220.0	1210.5
313.15	1090.0	1198.6	1232.2	1373.1	1094.0	1107.8	1216.6	1207.1
318.15	1087.0	1195.5	1228.8	1368.9	1090.7	1104.8	1213.2	1203.8
323.15	1084.0	1192.3	1225.5	1364.8	1087.4	1101.8	1210.0	1200.5
328.15	1081.0	1189.2	1222.2	1360.6	1084.2	1098.8	1206.8	1197.2
333.15	1078.0	1186.1	1218.9	1356.5	1081.0	1095.9	1203.7	1193.9
338.15	1075.0	1183.0	1215.6	1352.5	1077.8	1093.0	1200.6	1190.6
343.15	1072.1	1179.9	1212.3	1348.4	1074.7	1090.1	1197.6	1187.4
348.15	1069.2	1176.9	1209.1	1344.4	1071.6	1087.2	1194.5	1184.2
353.15	1066.3	1173.9	1205.9	1340.4	1068.5	1084.3	1191.5	1181.0
358.15	1063.4	1170.9	1202.8	1336.4	1065.4	1081.5	1188.5	1177.8
363.15	1060.6	1167.9	1199.7	1332.5	1062.3	1078.7	1185.5	1174.7

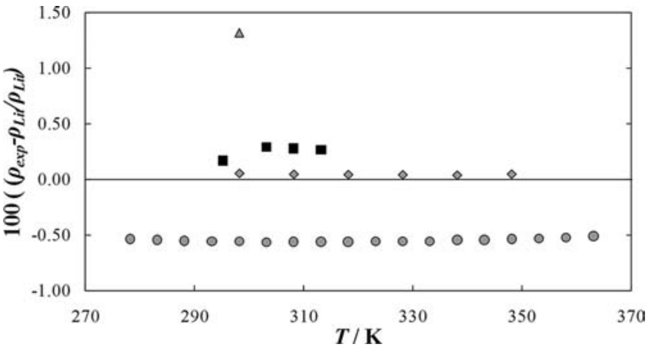


Figure 1. Relative deviations between the experimental density measured in this work (ρ_{exp}) and those reported in literature (ρ_{lit}) as a function of temperature for the ILs: ■, $[C_2mim][CF_3SO_3]$;[37] gray ●, $[C_2mim][N(CN)_2]$;[35] gray ◆, $[C_2mim][SCN]$;[34] gray ▲, $[C_2mim][Tos]$.[36]

uncertainty lower than $(2 \cdot 10^{-3})$ K. The temperature is typically controlled within a temperature fluctuation of $(\pm\ 5 \cdot 10^{-3})$ K, measured with a resolution better than $(1 \cdot 10^{-3})$ K. Samples were directly introduced into the flow cell (prism assembly) using a syringe; the flow cell was kept closed after sample injection. At least three independent measurements were taken for each sample and at each temperature. The refractive indices were measured with respect to air, and no corrections were applied. The ILs studied only show weak absorptions around 589 nm; hence they were considered as a nonabsorbing medium.

RESULTS AND DISCUSSION

Density. The experimental density data for the eight ILs considered in this work are presented in Table 3. Both $[C_2mim][Tos]$ and $[C_2mim][(OCH_3)_2PO_2]$ are solid at room temperature; thus, their density measurements were only carried out above 303.15 K.

Figure 1 displays the relative deviations between the data measured in this work and literature results.[34−37] The relative deviations on density values range between −0.56 % and 1.32 % for $[C_2mim][N(CN)_2]$ and $[C_2mim][Tos]$, respectively. These differences could be attributed to the purity of the ionic liquid, its water content, and the experimental technique used, among other factors. Nevertheless, a good agreement between our results and those reported by Vercher et al.[37] for $[C_2mim][CF_3SO_3]$ and by Domańska et al.[34] for $[C_2mim][SCN]$ is verified.

The density data measured in this work were used to widen the parameter table for the extension of the Ye and Shreeve group contribution method previously proposed by Gardas and Coutinho.[38] The ionic volume parameter for the anion thiocyanate, previously not available, was estimated based on the data gathered in this work combined with 60 experimental density values taken from literature for ILs with similar anions.[34,39,40] For the remaining anions, methylphosphonate, dimethylphosphate, and tosylate, their ionic volumes were determined based only on the density values reported in this work due to the lack of further data in literature. The new proposed ionic volumes are reported in Table 4 along with those previously reported by our group.[38,41] Figure 2 compares the experimental density data with the predicted density values based on the group contribution method[38] and their dependence on temperature. The predicted values are in good agreement with the experimental data, presenting maximum absolute relative deviations of 0.41 % for $[C_2mim][CH_3CO_2]$, 0.52 % for $[C_2mim][CH_3OHPO_2]$, 0.46 % for $[C_2mim][CH_3SO_3]$, 0.21 % for $[C_2mim][CF_3SO_3]$, 0.25 % for $[C_2mim][N(CN)_2]$, 0.49 % for $[C_2mim][SCN]$, 0.41 % for $[C_2mim][Tos]$, and 0.31 % for $[C_2mim][(OCH_3)_2PO_2]$. This method shows to be valuable in the prediction of density data for new ILs, when experimental data are still not available. The relative deviations between the experimental density data and those predicted for the entire temperature interval are reported in the Supporting Information (Figure S1).

For a common temperature, the density decreases with the following IL anion sequence: $[CF_3SO_3]^- > [CH_3SO_3]^- > [Tos]^- > [(OCH_3)_2PO_2]^- > [CH_3OHPO_2]^- > [SCN]^- > [N(CN)_2]^- > [CH_3CO_2]^-$. In general, fluorinated anions, toluenesulfonic-, phosphate-, and phosphonate-based anions present higher densities when compared to lower molecular weight anions, such as acetate, thiocyanate, and dicyanamide. The molecular weight of the anions $[CF_3SO_3]^-$, $[(OCH_3)_2PO_2]^-$, $[CH_3SO_3]^-$, $[Tos]^-$, $[CH_3OHPO_2]^-$, $[SCN]^-$, $[N(CN)_2]^-$, and $[CH_3CO_2]^-$ are (149.07, 125.04, 95.10, 171.19, 95.02, 58.08, 66.04, and 59.04) $g \cdot mol^{-1}$, respectively, and follow a close pattern to the

Table 4. Ionic Volumes, *V*, Determined with the Gardas and Coutinho Group Contribution Model[38]

ionic species	$V/Å^3$
Cation	
1,3-dimethylimidazolium[38]	154
Anion	
acetate[38]	86
methylphosphonate	78
methanesulfonate[41]	89
triflate[38]	129
dicyanamide[41]	72
thiocyanate	53
tosylate	57
dimethylphosphate	139
Additional Groups	
CH_2[38]	28

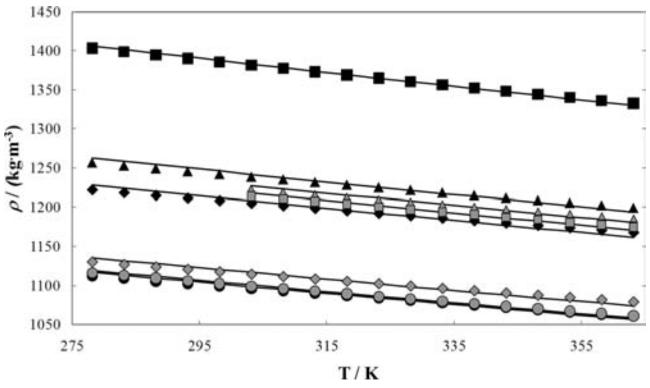


Figure 2. Experimental density (symbols) as a function of temperature (at 0.1 MPa) and respective description with the Gardas and Coutinho group contribution method[38] (lines) for the ILs: ●, $[C_2mim][CH_3CO_2]$; ♦, $[C_2mim][CH_3OHPO_2]$; ▲, $[C_2mim][CH_3SO_3]$; ■, $[C_2mim][CF_3SO_3]$; gray ●, $[C_2mim][N(CN)_2]$; gray ◆, $[C_2mim][SCN]$; gray ▲, $[C_2mim][Tos]$; gray ■, $[C_2mim][(OCH_3)_2PO_2]$.

density results obtained. The density dependence on the anion molecular weight was recently demonstrated by Kolbeck et al.[42] for a large number of IL anions, whose results highlighted a general trend on the density decrease with the decrease of the anion molecular weight.

The isobaric thermal expansion coefficients (α_p) of each IL were calculated using eq 1,

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p = -\left(\frac{\partial \ln\rho}{\partial T}\right)_p \qquad (1)$$

where ρ is the density in $\text{kg}\cdot\text{m}^{-3}$, T is the temperature in K, and p is the pressure in MPa.

The α_p values of all studied ILs are presented in Table 5, for the temperature of 308.15 K, and were calculated from the linear relationship between $\ln \rho$ and T using the experimental data measured. From the obtained values, it should be pointed out that no significant dependence of α_p on temperature was observed in the temperature range studied in this work. The α_p values displayed in Table 5 are in good agreement with literature data for $[C_2mim][CF_3SO_3]$[43] and $[C_2mim][SCN]$.[34] For the selected temperature, the α_p values follow the IL anion sequence: $[CF_3SO_3]^- > [N(CN)_2]^- > [CH_3CO_2]^- > [CH_3SO_3]^- > [SCN]^- > [(OCH_3)_2PO_2]^- > [CH_3OHPO_2]^- > [Tos]^-$.

Table 5. Thermal Expansion Coefficients, α_p, for the Studied Ionic Liquids at 308.15 K and at 0.1 MPa

	$10^4 (\alpha_p \pm \sigma^a)$
ionic liquid	K^{-1}
$[C_2mim][CH_3CO_2]$	5.550 ± 0.004
$[C_2mim][CH_3OHPO_2]$	5.284 ± 0.004
$[C_2mim][CH_3SO_3]$	5.440 ± 0.004
$[C_2mim][CF_3SO_3]$	6.047 ± 0.004
$[C_2mim][N(CN)_2]$	5.943 ± 0.004
$[C_2mim][SCN]$	5.426 ± 0.004
$[C_2mim][Tos]$	5.156 ± 0.004
$[C_2mim][(OCH_3)_2PO_2]$	5.399 ± 0.004

[a] Standard deviation.

Viscosity. The experimental dynamic viscosity data for the eight ionic liquids studied are presented in Table 6. The relative deviations between the data collected in this work and those reported in literature are depicted in Figure 3.[34,44−46] Larger differences are observed in the viscosity data compared to the density relative deviations among different authors. Viscosity measurements are nontrivial and are more affected by the presence of impurities (particularly water) than densities. The relative deviations of viscosity are in general below 10 %, with the exception of the data for the $[C_2mim][CH_3CO_2]$, where significant differences were observed. With this IL, both large

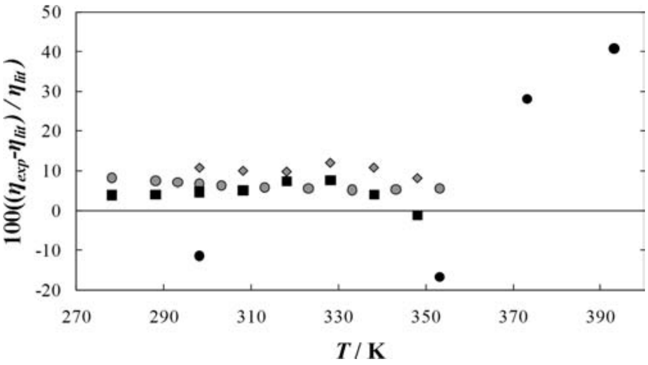


Figure 3. Relative deviations between the experimental viscosity measured in this work (η_{exp}) and those reported in literature (η_{lit}) as a function of temperature for the ILs: ●, $[C_2mim][CH_3CO_2]$;[44] ■, $[C_2mim][CF_3SO_3]$;[45] gray ●, $[C_2mim][N(CN)_2]$;[46] gray ◆, $[C_2mim][SCN]$.[34]

Table 6. Experimental Viscosity Values, η, for the Studied Ionic Liquids as a Function of Temperature and at 0.1 MPa

T	$\eta/(\text{mPa}\cdot\text{s})$							
K	$[C_2mim]$ $[CH_3CO_2]$	$[C_2mim]$ $[CH_3OHPO_2]$	$[C_2mim]$ $[CH_3SO_3]$	$[C_2mim]$ $[CF_3SO_3]$	$[C_2mim]$ $[N(CN)_2]$	$[C_2mim]$ $[SCN]$	$[C_2mim]$ $[Tos]$	$[C_2mim]$ $[(OCH_3)_2PO_2]$
278.15	723.62	916.06	805.33	99.825	32.507	54.573		
283.15	451.35	598.79	505.92	78.928	26.670	43.510		
288.15	295.70	406.82	336.04	63.507	22.233	35.360		
293.15	202.29	285.80	232.44	51.865	18.793	29.214		
298.15	143.61	206.76	166.59	42.936	16.088	24.505		
303.15	105.30	153.63	123.14	35.980	13.916	20.793	1417.4	192.68
308.15	79.324	116.89	93.482	30.482	12.159	17.858	842.45	144.32
313.15	61.327	90.832	72.642	26.087	10.718	15.493	531.73	110.51
318.15	48.415	71.925	57.617	22.527	9.5187	13.560	351.97	86.322
323.15	38.948	57.939	46.541	19.615	8.5175	11.970	242.85	68.641
328.15	31.873	47.385	38.203	17.208	7.6735	10.642	173.69	55.463
333.15	26.470	39.293	31.814	15.206	6.9511	9.5283	128.18	45.472
338.15	22.273	32.995	26.837	13.523	6.3268	8.5821	97.207	37.776
343.15	18.961	28.020	22.901	12.099	5.7883	7.7727	75.508	31.759
348.15	16.314	24.047	19.753	10.885	5.3188	7.0758	59.902	26.991
353.15	14.164	20.830	17.187	9.8447	4.9095	6.4717	48.424	23.167
358.15	12.407	18.199	15.083	8.9477	4.5485	5.9453	39.806	20.067
363.15	10.952	16.027	13.333	8.1695	4.2292	5.4846	33.215	17.528

Table 7. Correlation Parameters A_η, B_η, and $T_{0\eta}$ Obtained from the Vogel−Tammann−Fulcher Correlation Applied to the Viscosity Experimental Data

ionic liquid	A_η	B_η/K	$T_{0\eta}$/K
[C_2mim][CH_3CO_2]	−8.611	684.69	195.54
[C_2mim][CH_3OHPO_2]	−8.884	864.80	179.83
[C_2mim][CH_3SO_3]	−8.254	658.48	196.22
[C_2mim][CF_3SO_3]	−8.640	824.96	147.94
[C_2mim][$N(CN)_2$]	−8.319	581.69	158.02
[C_2mim][SCN]	−8.320	621.90	163.27
[C_2mim][Tos]	−8.357	685.48	224.41
[C_2mim][$(OCH_3)_2PO_2$]	−8.791	846.72	184.64

positive and negative relative deviations to the same data source are observed.[44] The reasons for such a disparity must be related to either the temperature control or the absorption of water during the experiments. In addition, the purity of the samples (that also include the preparation procedures), the measurement method employed, and sample handling are also additional factors that may explain the differences observed.

The Vogel−Tammann−Fulcher model, as described in eq 2, was used to correlate the experimental viscosity data,

$$\ln \eta = A_\eta + \frac{B_\eta}{(T - T_{0\eta})} \qquad (2)$$

where η is dynamic viscosity in Pa·s, T is the temperature in K, and A_η, B_η, and $T_{0\eta}$ are adjustable parameters. The parameters A_η, B_η, and $T_{0\eta}$, determined from the correlation of the experimental data for pure ILs, are presented in Table 7. The average absolute relative deviations between the experimental data and the correlated values are 0.42 % for [C_2mim][CH_3CO_2], 0.82 % for [C_2mim][CH_3OHPO_2], 0.27 % for [C_2mim][CH_3SO_3], 0.03 % for [C_2mim][CF_3SO_3], 0.11 % for [C_2mim][$N(CN)_2$], 0.05 % for [C_2mim][SCN], 0.24 % for [C_2mim][Tos], and 0.09 % for [C_2mim][$(OCH_3)_2PO_2$]. The relative deviations between the experimental data and those correlated for the entire temperature interval are reported in the Supporting Information (Figure S2).

The prediction of viscosities for the studied ILs was also carried out with the group contribution method previously proposed by Gardas and Coutinho,[47] which makes use of the Vogel−Tammann−Fulcher model described in eq 2. In this case, A_η and B_η are obtained by a group contribution method accordingly to the following equations,

$$A_\eta = \sum_{i=1}^{k} n_i a_{i,\eta} \qquad (3)$$

$$B_\eta = \sum_{i=1}^{k} n_i b_{i,\eta} \qquad (4)$$

where n_i is the number of groups of type i, k is the total number of different groups in the molecule, and $T_{0\eta}$ is taken as constant with a value of 165.06 K. Parameters $a_{i\eta}$ and $b_{i\eta}$ for the studied ILs are provided in Table 8. New values for these parameters for the ions $[Tos]^-$, $[CH_3OHPO_2]^-$, $[CH_3SO_3]^-$, $[SCN]^-$, and $[N(CN)_2]^-$ were estimated and are proposed here. These new parameters were estimated from the experimental viscosity values measured in this work along with additional experimental data reported in literature.[40,46,48]

Table 8. Group Contribution Parameters, $a_{i,\eta}$ and $b_{i,\eta}$, for the Group Contribution Method Proposed by Gardas and Coutinho[47] Based on the Vogel−Tammann−Fulcher Correlation

ionic species	$a_{i,\eta}$	$b_{i,\eta}$/K
	Cation	
1,3-dimethylimidazolium[47]	−7.271	510.51
	Anion	
acetate[47]	−2.739	618.50
methylphosphonate	−2.198	510.12
methanesulfonate	−2.406	510.44
triflate[47]	−1.150	176.97
dicyanamide	−1.263	46.60
thiocyanate	−0.925	55.52
tosylate	−4.551	1111.5
dimethylphosphate	−2.230	540.52
	Additional Groups	
CH_2[47]	$-7.528 \cdot 10^{-2}$	40.92

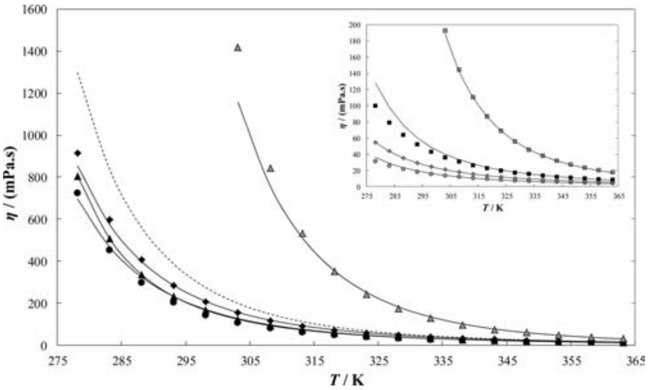


Figure 4. Experimental viscosity (symbols) as a function of temperature (at 0.1 MPa) and the group contribution method proposed by Gardas and Coutinho[47] (lines) for the ILs: ●, [C_2mim][CH_3CO_2]; ♦, [C_2mim][CH_3OHPO_2]; ▲, [C_2mim][CH_3SO_3]; ■, [C_2mim][CF_3SO_3]; gray ●, [C_2mim][$N(CN)_2$]; gray ◆, [C_2mim][SCN]; gray ▲, [C_2mim][Tos]; gray ■, [C_2mim][$(OCH_3)_2PO_2$]. The dashed line corresponds to [C_2mim][CH_3CO_2].

The description of the viscosity data using the group contribution model, applying eqs 3 and 4, along with the experimental data representation, is depicted in Figure 4. The average absolute relative deviations between the fitting and the experimental data are of 41.11 % for [C_2mim][CH_3CO_2], 2.34 % for [C_2mim][CH_3OHPO_2], 4.08 % for [C_2mim][CH_3SO_3], 7.08 % for [C_2mim][CF_3SO_3], 5.78 % for [C_2mim][$N(CN)_2$], 0.18 % for [C_2mim][SCN], 5.98 % for [C_2mim][Tos], and 0.93 % for [C_2mim][$(OCH_3)_2PO_2$]. The group contribution method provides, in general, a good prediction of the viscosity data. Nevertheless, large deviations are observed for the acetate-based ionic liquid. This is a particular example where more experimental data are in crucial need to allow further and proper predictions of the corresponding group contribution parameters.

The viscosity describes the internal resistance of a fluid toward a shear stress, and as it is well-known, ILs present higher viscosities than common molecular solvents. Since viscosity is dependent on intermolecular interactions (hydrogen-bonding,

Table 9. Heat Capacities, $C^{\circ}_{p,\mathrm{m}}$, at 298.15 K for the Studied Ionic Liquids

	$C^{\circ}_{p,\mathrm{m}}$	c°_{p}	$c^{\circ}_{p,\mathrm{V}}$ [a]	$C^{\circ}_{p,\mathrm{m}}$
ionic liquid	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot g^{-1}}$	$\mathrm{J \cdot K^{-1} \cdot cm^{-3}}$	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
		This Work		Literature
$[C_2mim][CH_3CO_2]$	321.90 ± 0.30	1.8912 ± 0.0018	2.0790 ± 0.0020	
$[C_2mim][CH_3OHPO_2]$	354.64 ± 0.81	1.7200 ± 0.0039	2.0783 ± 0.0047	
$[C_2mim][CH_3SO_3]$	345.52 ± 0.50	1.6751 ± 0.0024	2.0811 ± 0.0030	328 ± 36 (DSC)[48]
$[C_2mim][CF_3SO_3]$	362.80 ± 0.39	1.3941 ± 0.0015	1.9321 ± 0.0021	377 ± 49 (DSC)[49]
				362 ± 40 (DSC)[50]
				363.2 ± 11 (DSC)[51]
				380 ± 19 (DSC)[52]
				384 ± 19 (MDSC)[52]
				370 ± 18 (Tian-Calvet)[52]
$[C_2mim][N(CN)_2]$	314.64 ± 0.56	1.7755 ± 0.0032	1.9602 ± 0.0035	326 ± 42 (DSC)[49]
$[C_2mim][SCN]$	281.45 ± 0.66	1.6629 ± 0.0039	1.8575 ± 0.0044	287 ± 32 (DSC)[51]
$[C_2mim][(OCH_3)_2PO_2]$ [b]	411.78 ± 0.86	1.7433 ± 0.0036	2.1214 ± 0.0044	

[a] Derived volume-specific heat capacity, taking into account the density value at 298.15 K extrapolated from the linear fitting of the experimental density values as a function of temperature. [b] Subcooled liquid.

Table 10. Experimental Refractive Indices at the Sodium D-Line, n_D, for the Studied Ionic Liquids as a Function of Temperature and at 0.1 MPa

T	n_D							
K	$[C_2mim]$ $[CH_3CO_2]$	$[C_2mim]$ $[CH_3OHPO_2]$	$[C_2mim]$ $[CH_3SO_3]$	$[C_2mim]$ $[CF_3SO_3]$	$[C_2mim]$ $[N(CN)_2]$	$[C_2mim]$ $[SCN]$	$[C_2mim]$ $[Tos]$	$[C_2mim]$ $[(OCH_3)_2PO_2]$
288.37	1.50371	1.49534	1.49823	1.43572	1.51745			
293.28	1.50233	1.49390	1.49682	1.43432	1.51585			
298.19	1.50091	1.49249	1.49542	1.43296	1.51428			1.48175
303.10	1.49949	1.49115	1.49399	1.43159	1.51269			1.48050
308.01	1.49807	1.48982	1.49254	1.43025	1.51112			1.47909
312.91	1.49666	1.48854	1.49114	1.42886	1.50956			1.47771
317.82		1.48714						1.47636
322.73							1.53844	1.47511
325.68							1.53757	
327.64							1.53703	1.47384
329.61							1.53649	
332.55						1.53909	1.53570	
334.52						1.53850	1.53509	
336.48						1.53794	1.53461	
338.44						1.53739	1.53409	
340.41						1.53682	1.53356	
342.37						1.53636	1.53304	

dispersive, and Coulombic interactions), an increase in temperature will substantially decrease the intensity of H-bonding interactions, and therefore the viscosity decreases, as displayed in Figure 4. The experimental values depicted in Figure 4 show that the IL viscosities are largely dependent on the anion's nature. The viscosity of $[C_2mim]$-based ILs, at a fixed temperature, decreases in the following sequence: $[Tos]^-$ > $[(OCH_3)_2PO_2]^-$ > $[CH_3OHPO_2]^-$ > $[CH_3SO_3]^-$ > $[CH_3CO_2]^-$ > $[CF_3SO_3]^-$ > $[SCN]^-$ > $[N(CN)_2]^-$. This sequence is closely related with the intermolecular interactions that occur at the bulk liquid; yet, a molecular-based understanding of the ionic liquids' dominating interactions that could explain the viscosity trend is a challenging task. Their electrical charges, polarity, and molecular and electronic structure result in a multifaceted combination of specific interactions (Coulombic, van der Waals, hydrogen-bonding, and $\pi \cdots \pi$ interactions). In general, anions with an enhanced hydrogen bond acceptor character, such as $[CH_3OHPO_2]^-$, $[CH_3CO_2]^-$, and $[(OCH_3)_2PO_2]^-$, present higher viscosities.

Heat Capacity. The standard molar heat capacities obtained in this work and the available literature data for the studied ionic liquids,[48−52] at $T = 298.15$ K, are presented in Table 9. For the ionic liquids $[C_2mim][CH_3CO_2]$, $[C_2mim][CH_3OHPO_2]$, and $[C_2mim][(OCH_3)_2PO_2]$, no literature data were found. In this work, the heat capacity data were measured with a

Table 11. Refractive Indices of the Studied Ionic Liquids at 298.15 K, the Corresponding Temperature Derivative, $\mathrm{d}n_\mathrm{D}/\mathrm{d}T$, Calculated Molar Refractions, R_m, and the Calculated Free Volumes, f_m

ionic liquid	n_D (298.15 K)	$10^4 \cdot (\mathrm{d}n_\mathrm{D}/\mathrm{d}T)$ K^{-1}	R_m $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	f_m $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$
$[C_2mim][CH_3CO_2]$	1.50092	−2.88	45.61	109.22
$[C_2mim][CH_3OHPO_2]$	1.49250	−2.76	49.55	121.09
$[C_2mim][CH_3SO_3]$	1.49543	−2.90	48.45	117.57
$[C_2mim][CF_3SO_3]$	1.43297	−2.79	48.80	138.97
$[C_2mim][N(CN)_2]$	1.51429	−3.21	48.35	112.17
$[C_2mim][SCN]$	1.54871[a]	−2.81	48.18	103.34
$[C_2mim][Tos]$	1.54513[a]	−2.74		
$[C_2mim][(OCH_3)_2PO_2]$	1.48176[b]	−2.71		

[a] Values derived by linear extrapolation of the experimental data; all other data n_D (298.15 K) have been calculated via linear interpolation using the derivative $\mathrm{d}n_\mathrm{D}/\mathrm{d}T$ and the experimental result at 298.19 K, n_D (298.19 K). [b] Subcooled liquid.

considerable low uncertainty [(0.1 to 0.3) %], and our data differ from literature[48−52] less than 6 %. At 298.15 K, the molar heat capacities decrease with the following anion sequence: $[(CH_3O)_2PO_2]^- > [CF_3SO_3]^- > [CH_3OHPO_2]^- > [CH_3SO_3]^- > [CH_3CO_2]^- > [N(CN)_2]^- > [SCN]^-$. For each IL, the specific heat capacity, c_p°, and volume-specific heat capacity, $c_{p,\mathrm{V}}^\circ$, at 298.15 K were also derived, using the density values at the same temperature (from Table 3) and are presented in Table 9.

Refractive Index. The measured refractive index data are presented in Table 10; they cover the temperature range from (288 to 313) K, in steps of 5 K, while the temperature interval was scanned upward and downward. No temperature hysteresis effects were observed. The refractive indices of $[C_2mim][SCN]$, $[C_2mim][Tos]$, and $[C_2mim][(OCH_3)_2PO_2]$ were determined only at higher temperatures, since their refractive indices at lower temperatures exceeded the maximum range of the refractometer used ($n_\mathrm{D} = 1.54$), while $[C_2mim][Tos]$ and $[C_2mim][(OCH_3)_2PO_2]$ solidified at lower, yet not well-defined temperatures.

Refractive index literature data on the ionic liquids studied here are scarce. At 298.15 K, for $[C_2mim][CF_3SO_3]$, the value obtained here is nearly identical (relative deviation of −0.02 %) with the one found in literature,[53] while in the case of $[C_2mim][N(CN)_2]$ the relative deviations are lower than 0.3 %.[35]

As reported before[54] the refractive indices of ionic liquids are strongly dependent on the anion present, and the following trend was observed for the studied ILs: $[SCN]^- > [Tos]^- > [N(CN)_2]^- > [CH_3CO_2]^- > [CH_3SO_3]^- > [CH_3OHPO_2]^- > [(OCH_3)_2PO_2]^- > [CF_3SO_3]^-$.

For an overall comparison, the derived refractive indices of all ionic liquids, at T = 298.15 K, are compiled in Table 11 along with the observed temperature derivative of the refractive index, $\mathrm{d}n_\mathrm{D}/\mathrm{d}T$. The average absolute deviation of the derived refractive index is less than $7 \cdot 10^{-5}$ (cf. Table T1 in the Supporting Information).

In the temperature interval, any value of n_D, at a specific temperature, T, can be estimated using the following equation,

$$n_\mathrm{D}(T/\mathrm{K}) = n_\mathrm{D}(298.15\ \mathrm{K}) + \mathrm{d}n_\mathrm{D}/\mathrm{d}T(T/\mathrm{K} - 298.15\mathrm{K}) \tag{5}$$

The temperature dependence of the refractive index of each ionic liquid is very small and depends on the nature of the ionic liquid. For ILs, a decrease in the refractive index of 0.00027 to 0.00032 per kelvin is observed, which is less pronounced than that verified in most molecular solvents (ca. 0.00045 per K). The absolute deviation associated to the temperature derivative is less than $(5 \cdot 10^{-6})\ \mathrm{K}^{-1}$ (see the Supporting Information for further details).

Table 12. Group Contribution Parameters, a_{i,n_D} and b_{i,n_D}, for the Group Contribution Method According to Gardas and Coutinho[47] for the Calculation of Refractive Indices

ionic species	$a_{i,\eta}$	$b_{i,\eta}$/K
Cation		
1,3-dimethylimidazolium[47]	1.4436	$2.268 \cdot 10^{-4}$
Anion		
acetate	0.1387	$5.661 \cdot 10^{-5}$
methylphosphonate	0.1267	$4.461 \cdot 10^{-5}$
methanesulfonate	0.1338	$5.861 \cdot 10^{-5}$
triflate[47]	0.0783	$8.653 \cdot 10^{-5}$
dicyanamide	0.1619	$8.961 \cdot 10^{-5}$
thiocyanate	0.1844	$4.961 \cdot 10^{-5}$
tosylate	0.1787	$4.261 \cdot 10^{-5}$
dimethylphosphate	0.1145	$3.961 \cdot 10^{-5}$
Additional Groups		
CH_2[47]	0.0045	$4.587 \cdot 10^{-6}$

The derived molar refractions, R_m, and the free volumes, f_m, were additionally calculated and are displayed in Table 11. However, it should be remarked that R_m roughly represents the occupied part of the molar volume, and the restrictions of the applied model should be kept in mind.[53−55]

The prediction of the refractive indices for the studied ILs was also accomplished with the group contribution method proposed by Gardas and Coutinho,[47] which follows a linear function of the form,

$$n_\mathrm{D} = A_{n_\mathrm{D}} - B_{n_\mathrm{D}} T \tag{6}$$

where

$$A_{n_\mathrm{D}} = \sum_{i=1}^{k} n_i a_{i,n_\mathrm{D}} \tag{7}$$

$$B_{n_\mathrm{D}} = \sum_{i=1}^{k} n_i b_{i,n_\mathrm{D}} \tag{8}$$

where n_i is the number of groups of type i, and k is the total number of different groups in the molecule.

The estimated parameters $a_{i,nD}$ and $b_{i,nD}$ for the studied ILs are given in Table 12. New values for $a_{i,nD}$ and $b_{i,nD}$ for the ions $[SCN]^-$, $[Tos]^-$, $[N(CN)_2]^-$, $[CH_3CO_2]^-$, $[CH_3SO_3]^-$, $[CH_3OHPO_2]^-$, and $[(OCH_3)_2PO_2]^-$ were estimated and are proposed here.

CONCLUSIONS

The set of ionic liquids studied in this work was chosen, taking into account their potential in approaches regarding biomass dissolution. Aiming at gathering a complete database on the thermophysical properties of such ionic liquids, allowing therefore the design of related industrial processes, the density, viscosity, refractive index, isobaric thermal expansivity, and heat capacity of eight ionic liquids based on the cation 1-ethyl-3-methylimidazolium, combined with different anions, were determined. The impact of the IL anion on the properties studied was discussed, and novel parameters for the Gardas and Coutinho group contribution models are proposed.

Among the studied ionic liquids, $[C_2mim][CH_3CO_2]$ is still the best candidate for cellulose dissolution coupled to a low viscosity and density-favorable properties for further industrial applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Relative deviations between the experimental density (Figure S1) or viscosity (Figure S2) values and those predicted by the Gardas and Coutinho group contribution method and average absolute deviation of the refractive index and standard error in the estimate of the temperature derivative (Table T1). This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

Kenneth N. Marsh has been an inspiring figure for the authors of this work both through his activities as a researcher and as Editor of the *Journal of Chemical & Engineering Data*. His supportive attitudes and suggestions often helped us to enhance the quality of our work and persevere through some harsh criticism. This work which focuses on the main axis of research that Ken has led during the past decade on thermophysical properties, ionic liquids and cellulose solubility,[3−5] has been carried out with the main purpose to pay homage to the researcher and acknowledge him for his contribution to get where we are today.

REFERENCES

(1) Freire, C. S. R.; Silvestre, A. J. D.; Neto, C. P.; Cavaleiro, J. A. S. Lipophilic Extractives of the Inner and Outer Barks of Eucalyptus Globulus. *Holzforschung* **2002**, 372–379.

(2) Mäki-Arvela, P.; Anugwom, I.; Virtanen, P.; Sjöholm, R.; Mikkola, J. P. Dissolution of Lignocellulosic Materials and its Constituents Using Ionic Liquids — A Review. *Ind. Crops Prod.* **2010**, *32*, 175–201.

(3) Pinkert, A.; Marsh, K. N.; Pang, S.; Staiger, M. P. Ionic Liquids and their Interaction with Cellulose. *Chem. Rev.* **2009**, *109*, 6712–6728.

(4) Pinkert, A.; Marsh, K. N.; Pang, S. Alkanolamine Ionic Liquids and their Inability to Dissolve Crystalline Cellulose. *Ind. Eng. Chem. Res.* **2010**, *49*, 11809–11813.

(5) Pinkert, A.; Marsh, K. N.; Pang, S. Reflections on the Solubility of Cellulose. *Ind. Eng. Chem. Res.* **2010**, *49*, 11121–11130.

(6) Oliveira, F. S.; Freire, M. G.; Pratas, M. J.; Pauly, J.; Daridon, J. L.; Marrucho, I. M.; Coutinho, J. A. P. Solubility of Adamantane in Phosphonium-Based Ionic Liquids. *J. Chem. Eng. Data* **2009**, *55*, 662–665.

(7) Zakrzewska, M. E.; Bogel-Lukasik, E.; Bogel-Lukasic, R. Solubility of Carbohydrates in Ionic Liquids. *Energy Fuels* **2010**, *24*, 737–745.

(8) Rosatella, A. A.; Branco, L. C.; Afonso, C. A. M. Studies on Dissolution of Carbohydrates in Ionic Liquids and Extraction from Aqueous Phase. *Green Chem.* **2009**, *11*, 1406–1413.

(9) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of Cellulose with Ionic Liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.

(10) Xu, A.; Wang, J.; Wang, H. Effects of Anionic Structure and Lithium Salts Addition on the Dissolution of Cellulose in 1-Butyl-3-methylimidazolium-based Ionic Liquid Solvent Systems. *Green Chem.* **2010**, *12*, 268–275.

(11) Vitz, J.; Erdmenger, T.; Haensch, C.; Schubert, U. S. Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chem.* **2009**, *11*, 417–424.

(12) Freire, M. G.; Teles, A. R. R.; Ferreira, R. A. S.; Carlos, L. D.; Lopes-da-Silva, J. A.; Coutinho, J. A. P. Electrospun Nanosized Cellulose Fibers using Ionic Liquids at Room Temperature. *Green Chem.* **2011**, DOI:10.1039/C1GC15930E.

(13) Fukaya, Y.; Hayashi, K.; Wada, M.; Ohno, H. Cellulose Dissolution with Polar Ionic Liquids Under Mild Conditions: Required Factors for Anions. *Green Chem.* **2008**, *10*, 44–46.

(14) Sun, N.; Rahman, M.; Qin, Y.; Maxim, M. L.; Rodriguez, H.; Rogers, R. D. Complete Dissolution and Partial Delignification of Wood in the Ionic Liquid 1-Ethyl-3-methylimidazolium Acetate. *Green Chem.* **2009**, *11*, 646–655.

(15) Zavrel, M.; Bross, D.; Funke, M.; Büchs, J.; Spiess, A. C. High-throughput Screening for Ionic Liquids Dissolving (Ligno-)cellulose. *Bioresour. Technol.* **2009**, *100*, 2580–2587.

(16) Pu, Y.; Jiang, N.; Ragauskas, A. J. Ionic Liquid as a Green Solvent for Lignin. *J. Wood Chem. Technol.* **2007**, *27*, 23–33.

(17) Kilpeläinen, I.; Xie, H.; King, A.; Granstrom, M.; Heikkinen, S.; Argyropoulos, D. S. Dissolution of Wood in Ionic Liquids. *J. Agric. Food Chem.* **2007**, *55*, 9142–9148.

(18) Fort, D. A.; Remsing, R. C.; Swatloski, R. P.; Moyna, P.; Moyna, G.; Rogers, R. D. Can Ionic Liquids Dissolve Wood? Processing and Analysis of Lignocellulosic Materials with 1-*n*-Butyl-3-methylimidazolium Chloride. *Green Chem.* **2007**, *9*, 63–69.

(19) Zhao, H.; Baker, G. A.; Cowins, J. V. Fast Enzymatic Saccharification of Switchgrass after Pretreatment with Ionic Liquids. *Biotechnol. Prog.* **2010**, *26*, 127–133.

(20) Liu, L.; Chen, H. Enzymatic Hydrolysis of Cellulose Materials Treated with Ionic Liquid [BMIM] Cl. *Chin. Sci. Bull.* **2006**, *51*, 2432–2436.

(21) Dadi, A. P.; Varanasi, S.; Schall, C. A. Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step. *Biotechnol. Bioeng.* **2006**, *95*, 904–910.

(22) Sidhpuria, K. B.; Daniel-Da-Silva, A. L.; Trindade, T.; Coutinho, J. A. P. Supported Ionic Liquid Silica Nanoparticles (SILnPs) as an

Efficient and Recyclable Heterogeneous Catalyst for the Dehydration of Fructose to 5-Hydroxymethylfurfural. *Green Chem.* **2011**, *13*, 340–349.

(23) Zakrzewska, M. E.; Bogel-Łukasik, E.; Bogel-Łukasik, R. Ionic Liquid – Mediated Formation of 5-Hydroxymethylfurfural – A Promising Biomass-derived Building Block. *Chem. Rev.* **2011**, *111*, 397–417.

(24) Carvalho, P. J.; Regueira, T.; Santos, L.; Fernandez, J.; Coutinho, J. A. P. Effect of Water on the Viscosities and Densities of 1-Butyl-3-methylimidazolium Dicyanamide and 1-Butyl-3-methylimidazolium Tricyanomethane at Atmospheric Pressure. *J. Chem. Eng. Data* **2010**, *55*, 645–652.

(25) Neves, C.; Batista, M. L. S.; Claudio, A. F. M.; Santos, L.; Marrucho, I. M.; Freire, M. G.; Coutinho, J. A. P. Thermophysical Properties and Water Saturation of [PF_6]-Based Ionic Liquids. *J. Chem. Eng. Data* **2010**, *55*, 5065–5073.

(26) Oliveira, F. S.; Freire, M. G.; Carvalho, P. J.; Coutinho, J. A. P.; Lopes, J. N. C.; Rebelo, L. P. N.; Marrucho, I. M. Structural and Positional Isomerism Influence in the Physical Properties of Pyridinium NTf_2-Based Ionic Liquids: Pure and Water-Saturated Mixtures. *J. Chem. Eng. Data* **2010**, *55*, 4514–4520.

(27) Suurkuusk, J.; Wadsö, I. Design and Testing of an Improved Precise Drop Calorimeter for the Measurement of the Heat Capacity of Small Samples. *J. Chem. Thermodyn.* **1974**, *6*, 667–679.

(28) Santos, L. M. N. B. F.; Rocha, M. A. A.; Rodrigues, A. S. M. C.; Štejfa, V.; Fulem, M.; Bastos, M. Reassemble and Test of High-Precision Heat Capacity Drop Calorimeter. Heat Capacities at 298.15 K of Some Polyphenyls. *J. Chem. Thermodyn.* **2011**, DOI:10.1016/j.jct.2011.06.010.

(29) Konicek, J.; Suurkuusk, J.; Wadsö, I. A Precise Drop Heat Capacity Calorimeter for Small Samples. *Chem. Scr.* **1971**, *1*, 217–220.

(30) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Leitão, M. L. P.; Roux, M. V.; Torres, L. A. Reference Materials for Calorimetry and Differential Thermal Analysis. *Thermochim. Acta* **1999**, *331*, 93–204.

(31) Chirico, R. D.; Diky, V.; Magee, J. W.; Frenkel, M.; Marsh, K. N. Thermodynamic and Thermophysical Properties of the Reference Ionic Liquid: 1-Hexyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]-amide (Including Mixtures). Part 2. Critical Evaluation and Recommended Property Values. *Pure Appl. Chem.* **2009**, *81*, 791–828.

(32) Blokhin, A. V.; Paulechka, Y. U.; Kabo, G. J. Thermodynamic Properties of [C_6mim][NTf_2] in the Condensed State. *J. Chem. Eng. Data* **2006**, *51*, 1377–1388.

(33) Shimizu, Y.; Ohte, Y.; Yamamura, Y.; Saito, K.; Atake, T. Low-Temperature Heat Capacity of Room-Temperature Ionic Liquid, 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide. *J. Phys. Chem. B* **2006**, *110*, 13970–13975.

(34) Domańska, U.; Królikowska, M.; Królikowski, M. Phase Behaviour and Physico-chemical Properties of the Binary Systems {1-Ethyl-3-methylimidazolium Thiocyanate, or 1-Ethyl-3-methylimidazolium Tosylate + Water, or + an Alcohol}. *Fluid Phase Equilib.* **2010**, *294*, 72–83.

(35) Fröba, A. P.; Kremer, H.; Leipertz, A. Density, Refractive Index, Interfacial Tension, and Viscosity of Ionic Liquids [EMIM][$EtSO_4$], [EMIM][NTf_2], [EMIM][$N(CN)_2$], and [OMA][NTf_2] in Dependence on Temperature at Atmospheric Pressure. *J. Phys. Chem. B* **2008**, *112*, 12420–12430.

(36) Hernández-Fernández, F. J.; Ríos, A. P.; Gómez, D.; Rubio, M.; Tomás-Alonso, F.; Víllora, G. Ternary Liquid-liquid Equilibria for Mixtures of an Ionic Liquid + *n*-Hexane + an Organic Compound Involved in the Kinetic Resolution of Rac-1-phenyl Ethanol (Rac-1-phenyl Ethanol, Vinyl Propionate, Rac-1-phenylethyl Propionate or Propionic Acid) at 298.2 K and Atmospheric Pressure. *Fluid Phase Equilib.* **2008**, *263*, 190–198.

(37) Vercher, E.; Llopis, F. J.; González-Alfaro, M. V.; Martínez-Andreu, A. Density, Speed of Sound, and Refractive Index of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate with Acetone, Methyl Acetate, and Ethyl Acetate at Temperatures from (278.15 to 328.15) K. *J. Chem. Eng. Data* **2009**, *55*, 1377–1388.

(38) 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.

(39) Domańska, U.; Laskowska, M. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of {1-Butyl-3-methylimidazolium Thiocyanate + 1-Alcohols}. *J. Chem. Eng. Data* **2009**, *54*, 2113–2119.

(40) Sánchez, L. G.; Espel, J. R.; Onink, F.; Meindersma, G. W.; Haan, A. B. Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2009**, *54*, 2803–2812.

(41) Tomé, L. I. N.; Gardas, R. L.; Carvalho, P. J.; Pastoriza-Gallego, M. J.; Piñeiro, M. M.; Coutinho, J. A. P. Measurements and Correlation of High-Pressure Densities of Phosphonium Based Ionic Liquids. *J. Chem. Eng. Data* **2011**, *56*, 2205–2217.

(42) Kolbeck, C.; Cremer, T.; Lovelock, K. R. J.; Paape, N.; Schulz, P. S.; Wasserscheid, P.; Maier, F.; Steinrück, H. P. Influence of Different Anions on the Surface Composition of Ionic Liquids Studied Using ARXPS. *J. Phys. Chem. B* **2009**, *113*, 8682–8688.

(43) Vercher, E.; Orchillés, A. V.; Miguel, P. J.; Martínez-Andreu, A. Volumetric and Ultrasonic Studies of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate Ionic Liquid with Methanol, Ethanol, 1-Propanol, and Water at Several Temperatures. *J. Chem. Eng. Data* **2007**, *52*, 1468–1482.

(44) Fendt, S.; Padmanabhan, S.; Blanch, H. W.; Prausnitz, J. M. Viscosities of Acetate or Chloride-based Ionic Liquids and Some of Their Mixtures with Water or Other Common Solvents. *J. Chem. Eng. Data* **2011**, *56*, 31–34.

(45) Rodríguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155.

(46) Schreiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. Fractional Walden Rule for Ionic Liquids: Examples from Recent Measurements and a Critique of the So-called Ideal KCl Line for the Walden Plot. *J. Chem. Eng. Data* **2009**, *55*, 1784–1788.

(47) 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*, 1274–1290.

(48) 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.

(49) Yu, Y.-H.; Soriano, A. N.; Li, M.-H. Heat Capacities and Electrical Conductivities of 1-Ethyl-3-methylimidazolium-based Ionic Liquids. *J. Chem. Thermodyn.* **2009**, *41*, 103–108.

(50) Ficke, L. E.; Rodríguez, H.; Brennecke, J. F. Heat Capacities and Excess Enthalpies of 1-Ethyl-3-methylimidazolium-Based Ionic Liquids and Water. *J. Chem. Eng. Data* **2008**, *53*, 2112–2119.

(51) García-Miaja, G.; Troncoso, J.; Romaní, L. Excess Properties for Binary Systems Ionic Liquid + Ethanol: Experimental Results and Theoretical Description Using the ERAS Model. *Fluid Phase Equilib.* **2008**, *274*, 59–67.

(52) Diedrichs, A.; Gmehling, J. Measurement of Heat Capacities of Ionic Liquids by Differential Scanning Calorimetry. *Fluid Phase Equilib.* **2006**, *244*, 68–77.

(53) Vercher, E.; Llopis, F. J.; González-Alfaro, V.; Martínez-Andreu, A. Refractive Indices and Deviations in Refractive Indices for Binary Mixtures of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate with Methanol, Ethanol, 1-Propanol, and 2-Propanol at Several Temperatures. *J. Chem. Eng. Data* **2009**, *55*, 1430–1433.

(54) Tariq, M.; Forte, P. A. S.; Gomes, M. F. C.; Lopes, J. N. C.; Rebelo, L. P. N. Densities and Refractive Indices of Imidazolium- and Phosphonium-based Ionic Liquids: Effect of Temperature, Alkyl Chain Length, and Anion. *J. Chem. Thermodyn.* **2009**, *41*, 790–798.

(55) Shimizu, K.; Tariq, M.; Gomes, M. F. C.; Rebelo, L. P. N.; Lopes, J. N. C. Assessing the Dispersive and Electrostatic Components of the Cohesive Energy of Ionic Liquids Using Molecular Dynamics Simulations and Molar Refraction Data. *J. Phys. Chem. B* **2010**, *114*, 5831–5834.