The effect of dissolved water on the viscosities of hydrophobic room-temperature ionic liquids†

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Data for viscosity *vs.* water content for three hydrophobic room-temperature ionic liquids show that their viscosities are strongly dependent on the amount of dissolved water.

Room-temperature ionic liquids (RTILs) are salts that melt at or below room temperature.[1] RTILs are being considered for a wide variety of applications, including separations and electrochemical technologies, and as "green" alternatives to volatile organic solvents.[1–4] One impediment to the use of RTILs is the shortage of reliable physical property data for these interesting materials.[5] The current situation is illustrated by viscosity data for 1-butyl-3-methylimidazolium hexafluorophosphate, $[C_4mim][PF_6]$. Several groups have reported viscosity measurements at 1 bar in the range 283–363 K. Although the reported uncertainties in the viscosity data are claimed to be 3% or less,[6–9] the literature data differ by 30% or more over most of that temperature range (see Fig. S1, ESI†). For example, at 293.15 K, the published values for the viscosity of $[C_4mim][PF_6]$ are 430 mPa s,[5] 371 mPa s,[6] 318 mPa s,[7] 308 mPa s,[10] 286 mPa s,[11] and 201 mPa s.[9]

Our hypothesis is that the disagreement in the viscosity (and other physical property) data for RTILs is due primarily to inconsistent sample purity. The viscosity of an RTIL is, of course, affected by the presence of impurities. For example, the presence of water and organic solvents has been shown to decrease the viscosity of RTILs,[12–14] and the presence of chloride has been shown to increase the viscosity of RTILs.[12] Note, however, that little is known about the quantitative effect of low levels of water on physical properties. Water is the most insidious impurity because of its ubiquity. Even "hydrophobic" RTILs, which are not miscible with water, rapidly absorb water from the atmosphere[12,15–17] or from moist surfaces. Hence, unless an RTIL is carefully dried and handled, it will be contaminated with water.

To test the effect of low levels of water contamination on viscosity, we dried the following three hydrophobic RTILs to $\leqslant$30 ppm water ($\leqslant$0.003 mass%): $[C_4mim][PF_6]$; 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $[C_4mim][Tf_2N]$; and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, $[C_2mim][Tf_2N]$.‡ Then we measured the kinematic viscosity (ν) *vs.* water content at atmospheric pressure and 293.15 K with an open gravitational capillary viscometer.§ With this technique one measures the time (t) required for a given volume of the liquid to flow through a capillary under the influence of gravity. The flow time is proportional to the kinematic viscosity, $\nu = Ct$, where the proportionality constant, C, is determined by calibration. The absolute viscosity (η) is related to ν by the density (ρ) of the liquid, $\eta = \nu\rho$. The following RTIL densities at 293.15 K and 1 bar were used: $\rho([C_4mim][PF_6]) = 1372.7\ \mathrm{kg\ m^{-3}}$,[6] $\rho([C_4mim][Tf_2N]) = 1442.5\ \mathrm{kg\ m^{-3}}$,[18] and $\rho([C_2mim][Tf_2N]) = 1524.3\ \mathrm{kg\ m^{-3}}$.[18]

The capillary viscometer must be open to the atmosphere to function properly, but atmospheric moisture was effectively excluded by connecting desiccant-filled tubes to the openings. All glassware was oven-dried, and transfers were performed under argon or nitrogen. A key to these experiments is that the water content of the RTIL was determined before *and after* each viscosity measurement by coulometric Karl Fischer (KF) titration.¶ A check of the water content after a viscosity measurement is important because it is the only way to ensure that the water content has not changed significantly. To our knowledge, this is the first time such a precaution has been reported when making a physical property measurement for an RTIL. We recommend that this precaution be generally adopted.

The data for viscosity *vs.* water content are given in Table 1. The viscosities of all three RTILs decrease rapidly with increasing water content. For each RTIL, the percent change in viscosity with increasing water content is plotted in Fig. 1. The rate of decrease was largest for $[C_4mim][PF_6]$—its kinematic viscosity decreased by 17% with the addition of only 1900 ppm (0.19%) water. Clearly, one must dry and handle $[C_4mim][PF_6]$ carefully if one hopes to obtain reliable viscosity data since even a 100 ppm (0.01%) change in water content leads to a change in viscosity of about 1%. The change in viscosity is smaller for $[C_4mim][Tf_2N]$ and $[C_2mim][Tf_2N]$, but is still dramatic; their viscosities decrease by about 30% with the addition of only 1% (by mass) water. Because of the magnitude of this water effect, viscosity data for RTILs are suspect unless the water content is determined before *and after* the viscosity measurement.

Disagreement between sets of published viscosities of RTILs could be due to water contamination, but it could also be due to one or more of the following causes: impurities from the synthesis (*e.g.*, chloride) or from RTIL decomposition; an inappropriate working equation for the viscometer (as discussed in ref. 19); an improper calibration of the viscometer; or an inconsistent experimental technique. While there is not enough information in the literature to completely rule out any of these possibilities, the published data are consistent with water contamination being the

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† Electronic supplementary information (ESI) available: a table of the viscosity measurements showing the kinematic viscosity, initial and final water content, average water content, average mole fraction of water, and percent change in kinematic viscosity; for $[C_4mim][PF_6]$ a plot of the percent deviation of literature viscosities from a viscosity *vs.* temperature correlation; and graphs of the literature data of the viscosity *vs.* temperature for all three RTILs. See http://www.rsc.org/suppdata/cc/b4/b417348a/

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Table 1 Viscosity *vs.* water content data at 293.15 K and atmospheric pressure

Ionic liquid	Absolute viscosity/mPa s	Average H_2O content[a]/ppm by mass
$[C_4mim][Tf_2N]$	63.5	10
	63.1	150
	62.4	400
	61.0	900
	58.8	1740
	53.5	4020
	42.6	10480
$[C_2mim][Tf_2N]$	39.4	10
	39.3	130
	38.8	480
	38.1	1010
	36.6	1980
	33.8	4180
	29.4	8450
	26.2	12590
$[C_4mim][PF_6]$	394	30
	388	180
	375	470
	358	990
	328	1900

[a] The average of the water contents before and after measuring viscosity. See Table S1 of the ESI for the raw data.

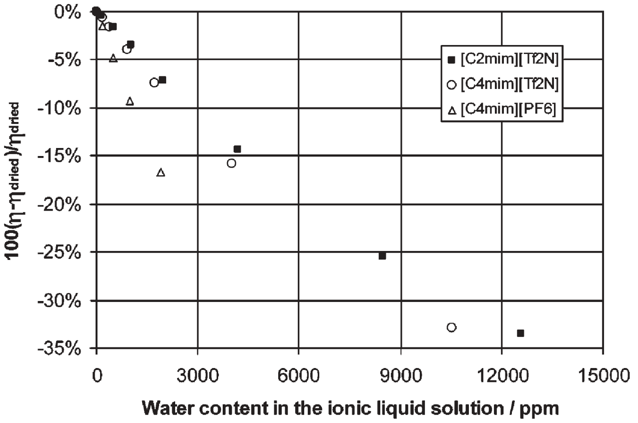

Fig. 1 Percent change in the absolute viscosity *vs.* water content for $[C_2mim][Tf_2N]$, $[C_4mim][Tf_2N]$ and $[C_4mim][PF_6]$.‡,§

primary problem. As mentioned above, unless an RTIL is carefully dried and handled, it will be contaminated with water. Water contamination decreases the viscosity; therefore, we expect published viscosities to be no greater than the viscosities we obtained for our driest samples. This is generally observed, though there are a few exceptions that cannot be explained by water contamination (see the ESI† for further details). Chloride contamination would lead to higher viscosities than those we obtained, which is typically not the case. Another strong point in favor of water contamination as the cause for discrepancies is that the magnitude of the discrepancies nicely agrees with the magnitude of the viscosity changes caused by water. That is, the change in viscosity with water content is large enough to explain all of the lower published values of viscosity (keeping in mind that 1900 ppm water is well below the saturation limit of $[C_4mim][PF_6]$[17]). Also, the largest discrepancies in the literature are for $[C_4mim][PF_6]$ (see the ESI† for further details), which is expected since water causes a greater change in the viscosity of this RTIL than in the viscosities of the other two RTILs, Fig. 1.

Although we investigated only three RTILs, we anticipate that the behavior of other RTILs will be similar since the magnitude of the effect of water probably arises, in part, from the relatively high viscosity of RTILs compared to water. This work focuses on viscosity, but similar implications exist for some other physical properties of RTILs. For example, using the Stokes–Einstein and Nernst–Einstein equations as a basis for prediction, we anticipate that changes in electrolytic conductivity with water content will be of a similar percent magnitude. We are currently investigating this prediction.

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Notes and references

‡ All three RTILs were commercially obtained. They were dried with stirring on a vacuum line with a mechanical pump and a liquid nitrogen trap. The $[C_4mim][Tf_2N]$ and $[C_2mim][Tf_2N]$ were heated to about 60 °C during drying, but $[C_4mim][PF_6]$ was dried at room temperature to avoid hydrolysis of the anion. Karl Fischer titration was used to monitor the drying process. For all three RTILs the manufacturer's claim of <50 ppm chloride was verified with negative $AgNO_3$ tests and with chloride-selective electrode measurements. The purity of each RTIL was also checked by ^1H and ^{19}F NMR. To ensure that neither contamination nor decomposition occurred during the viscosity measurements, NMR spectra were obtained after drying each RTIL and after the completion of the viscosity *vs.* water content measurements. In every case, >99.5% of the total peak integral in the ^1H and ^{19}F NMR spectra was due to the RTIL (*i.e.*, <0.5% of the total peak integral was from impurity peaks).

§ For the kinematic viscosity measurements we used the procedure outlined in ASTM test method D 445–03; however, instead of averaging two determinations of the kinematic viscosity, at least four determinations were averaged for each entry in Table 1. Commercially obtained Ubbelohde capillary viscometers were used for all the measurements. During a measurement, the viscometers were immersed in an insulated, continuously stirred bath (ethylene glycol + water) whose temperature was regulated with a refrigerated circulator, an electric heater, and a precision temperature controller. The uncertainty in the bath temperature, which was measured with an ITS-90 calibrated platinum resistance thermometer, is estimated to be ± 0.02 K, which corresponds to a standard uncertainty of $\leqslant 0.10\%$ in the viscosity measurement. For each capillary, the calibration constant, *C*, was determined using standard reference liquids. The standard uncertainty in *C* is estimated to be 0.48%, which corresponds to a standard uncertainty of 0.48% in the viscosity measurements. Flow times were measured automatically with an optical sensor; this measurement does not contribute significantly to the uncertainty of the viscosity measurement. Hence, with this viscometer, the expanded uncertainty ($k = 2$) in the kinematic viscosity measurements is estimated to be 1%. The Hagenbach (kinetic energy) correction was <0.003%. No correction was made to account for the difference in surface tension between the hydrocarbon-based calibration liquids and the RTILs.

¶ Uncertainties in the water determination were estimated by making measurements on 100 ppm, 1000 ppm, and 10 000 ppm water standards. Not surprisingly, the uncertainty in the determination of water content changes significantly as a function of the concentration. At 100 ppm water content, the expanded uncertainty ($k = 2$) of the water content determinations is estimated to be 20% (that is, $[100 \pm 20]$ ppm); at 1000 ppm water content, the expanded uncertainty is 6%; and at 10 000 ppm water content, the expanded uncertainty is 4%.

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