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Expanding the polarity range of ionic liquids

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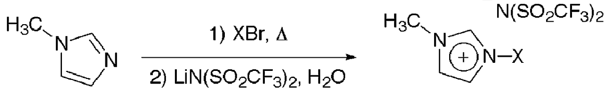
Abstract—The polarity of several [X-mim]NTf_2 ionic liquids, as measured with solvatochromic dyes, Reichardt's dye and Nile Red, may be varied over a wide range by attachment of functional group-containing substituents (X) to the imidazolium cation.

Air- and water-stable room-temperature ionic liquids (RTILs) have emerged as a powerful alternative to conventional molecular organic solvents.[1] Undetectable vapor pressure, as well as ease of recovery and reuse, make RTILs a greener alternative to volatile organic solvents.[2] An intriguing aspect is the ability to influence various physical properties by varying the RTIL structure. Thus, RTILs have been described as 'designer-solvents.'[3]

The polarity of RTILs is an area of current research interest. Both solvatochromic and fluorescent dyes have been utilized to determine the polarity of these solvents.[4] However, unlike other physical properties of RTILs, such as phase transition temperatures, viscosity, etc., which vary over wide ranges,[5] only small polarity changes are reported. Thus, the polarity of 1-alkyl-3-methylimidazolium tetrafluoroborates does not change appreciably when the 1-alkyl group is elongated.[6] Varying the anion has a somewhat greater effect. However, changing the anion alters an array of RTIL physical properties including their physical state, as well as miscibility with molecular solvents.



Ionic Liquid	X	Abbreviation
1	C_3H_7	[C_3-mim]NTf_2
2	$C_{10}H_{21}$	[C_{10}-mim]NTf_2
3	$C_6H_5CH_2$	[$C_6H_5CH_2$-mim]NTf_2
4	$CH_3O(CH_2)_2$	[$CH_3O(CH_2)_2$-mim]NTf_2
5	$HO(CH_2)_2$	[$HO(CH_2)_2$-mim]NTf_2

Scheme 1. Synthesis of RTILs.

A few isolated examples of 1-X-3-alkylimidazolium salts are reported in which X contains a functional group.[7] However, the influence of incorporating a functional group on the polarity of such RTILs is unknown.

To evaluate the potential of functional group variation for producing significant polarity changes in RTILs, a series of 1-X-3-methylimidazolium bis(trifluoromethylsulfonyl)imides, [X-mim]NTf_2, **1**–**5** was prepared by reaction of 1-methylimidazole and the appropriate organic bromides, followed by anion metathesis with $LiN(SO_2CF_3)_2$ in water (Scheme 1).[5,6a]

For this series of water-immiscible RTILs, NTf_2^- was selected as the anion instead of PF_6^- due to the anticipated lower viscosity and lower phase transitions of the bis(trifluoromethylsulfonyl)imide ionic liquids.[5] Compounds **1**–**5** are free-flowing liquids at room temperature. These RTILs were stored in capped vials on the bench top without special precaution. Their physical properties are given in Table 1. The water content is consistent with atmospheric moisture saturation of the RTILs through the contact with air.[9]

Polarities of RTILs **1**–**5** as measured with Reichardt's dye[10] and Nile Red[11] are given in Table 2. As can be seen, changing the X group produces a range of $E_T(30)$ values from 61.4 kcal/mol for hydroxy-containing RTIL **5** to 51.0 kcal/mol for [C_{10}-mim]NTf_2 (**2**) for the undried samples. To our knowledge, this is the largest polarity range obtained to date for a series of structurally related RTILs. In general, the trend follows the

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Table 1. Selected physical properties of RTILs

RTIL	T_g (T_m) (°C)[a]	*d* (g/ml)[b]	Water content (ppm)[c]
1	-87	1.473	3810
2	-83 (-29, -2)	1.271	1450
3	-56	1.491	2180
4	-81	1.509	3050
5	-79	1.572	3380

[a] Determined by DSC on heating with a Shimadzu DSC-50 equipped with a low-temperature unit, according to a literature procedure.[8]

[b] Obtained with an Anton-PAAR density measuring system at 25.0±0.1°C.

[c] Determined by a Metler-Toledo DL36 KF Coulometer with Aqua Star Coulomat A and Coulomat C solutions as an average of two runs with values that agreed within 5%.

polarity of the functional group in the substituent X. With Nile Red, changes in E_{NR} values are smaller, but follow the same trend.

To evaluate a potential effect of water on the polarity, ionic liquids **1** and **5** were dried under vacuum (0.15 torr) for 48 hours and the water content and polarity were measured immediately after each sample was removed from the vacuum. Higher water content of the dried ionic liquid **5** (390 ppm), as compared to dried **1** (160 ppm), is probably due to the hydrogen bonding between the hydroxy-group of the ionic liquid and water molecules, which prevents further removal of water from the former. Based on the data given in Tables 1 and 2, ionic liquid **1** appears to absorb more moisture than the remainder of the ionic liquids.

As shown by the spectroscopic data for ionic liquids **1** and **5** in Table 2, variation of the water content has little effect on the polarity of these ionic liquids, which is consistent with literature observations.[5a] This establishes that the position of the dye absorption band is controlled by the functional group-containing substituent on the imidazolium cation and not the amount of water present in the RTIL.

Table 2. Spectroscopic data obtained with solvatochromic dyes and the calculated polarities in parentheses

RTIL	λ_{max} (nm)[a] (E_T(30), (kcal/mol))	λ_{max} (nm)[a] (E_{NR} (kcal/mol))
1	550.0 (52.0)	547.5 (52.2)
1 (dried)[b]	550.5 (51.9)	547.0 (52.3)
2	560.5 (51.0)	547.5 (52.2)
3	546.0 (52.4)	552.0 (51.8)
4	528.0 (54.1)	561.0 (51.0)
5	465.5 (61.4)	566.0 (50.5)
5 (dried)[c]	470.0 (60.8)	565.0 (50.6)

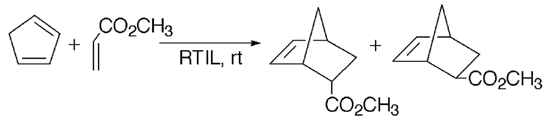
[a] λ_{max} values were recorded on a Shimadzu UV 2401-PC spectrophotometer under conditions similar to those given in Ref. 6.

[b] Water content was 160 ppm as determined by Karl–Fisher titration.

[c] Water content was 390 ppm as determined by Karl–Fisher titration.

Diels–Alder reactions are among the most useful synthetic processes for carbon–carbon bond formation. RTILs have been shown to be suitable media for Diels–Alder reactions[12] and have been used as both solvents and catalysts for such reactions.

The *endo*/*exo* ratio of Diels–Alder reaction products can be related to the polarity of molecular organic solvents in which the reaction is performed.[13] Therefore, a study of a Diels–Alder reaction (Scheme 2) in RTILs **1**–**5** was undertaken to probe the influence of ionic solvent polarity on the *endo*/*exo* ratio.



Scheme 2. The Diels–Alder reaction.

This Diels–Alder reaction of cyclopentadiene and methyl acrylate is reported to be heterogeneous in 1-alkyl-3-methylimidazolium RTILs[14] with the *endo*/*exo* ratio depending on both the concentration of the reactants and the reaction time. In our case, the reactions were homogeneous. The influence of concentration and reaction time was evaluated for ionic liquid **1**. Over a range of concentrations (0.3–1 M) and reaction times (2–24 h), no change in the *endo*/*exo* product ratio was observed.

The reactions were conducted by dissolving freshly distilled cyclopentadiene and an equimolar amount of methyl acrylate in 2.0 ml of the RTIL at room temperature and stirring for 2 h. The products were extracted with hexane and analyzed by GC or in the case of $[C_{10}\text{-mim}]NTf_2$ by ^1H NMR spectroscopy,[15] since RTIL **2** is slightly soluble in hexane. Yields in all cases were >95% as determined by ^1H NMR spectroscopy. Results from reaction of cyclopentadiene with methyl acrylate in RTILs **1**–**5** are presented in Table 3 together with literature data for comparison.

Although the variation in the *endo*/*exo* ratio is modest, a correlation with the polarity of the ionic liquid is

Table 3. Comparison of the RTILs polarity and stereoselectivity of the Diels–Alder reaction of cyclopentadiene with methyl acrylate

RTIL	E_T(30) (kcal/mol)	*endo*/*exo*[a]
$[C_3\text{-mim}]NTf_2$	52.0	4.3
$[C_{10}\text{-mim}]NTf_2$	52.1	4.3[b]
$[C_6H_5CH_2\text{-mim}]NTf_2$	52.5	4.9
$[CH_3O(CH_2)_2\text{-mim}]NTf_2$	54.1	5.7
$[HO(CH_2)_2\text{-mim}]NTf_2$	61.4	6.1
$[C_4\text{-mim}]BF_4$	52.5[c]	4.3[d]
$[Et_3NH]NO_3$	61.6[e]	6.7[d]

[a] Determined by GC.

[b] Determined by ^1H NMR spectroscopy.

[c] Ref. 5b.

[d] Ref. 14.

[e] Ref. 10.

readily evident with greater polarity producing a higher *endo*/*exo* ratio. The similarity in the *endo*/*exo* ratio of $[HO(CH_2)_2\text{-mim}]NTf_2$ and that reported for $[Et_3NH]NO_3$ ionic liquid is attributed to a dominant role of H–O and H–N interactions, respectively, as opposed to the weaker H–C interactions present in RTILs **1**–**4** and $[C_4\text{-mim}]BF_4$.[14]

In conclusion, incorporation of functional groups into the X substituent of 1-X-3-methylimidazolium bis(trifluoromethylsulfonyl)imides markedly expands the polarity range for such ionic liquids. We are currently exploring the effects of other functional groups on the polarity of ionic liquids and their applications in organic synthesis.

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