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# How polar are room-temperature ionic liquids?

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**The solvent strength and polarity of four imidazolium and pyridinium based ionic liquids, as measured using two different fluorescent probes, indicate that these liquids are more polar than acetonitrile but less polar than methanol.**

The realization that pollution prevention is frequently more cost effective than remediation has catalyzed tremendous effort in the development of environmentally benign solvents and processes. Room-temperature ionic liquids (ILs) are one such class of solvents. They are organic molten salts that in their pure state are liquids at temperatures around ambient. The typical IL is based on a bulky *N*-alkylpyridinium or *N,N′*-dialkylimidazolium cation, with a variety of substituents paired with a variety of anions. These, along with alkylammonium and alkylphosphonium compounds, are most popular.[1] Interestingly, even though ILs are organic solvents, they exhibit vanishingly small vapor pressures.[2,3]

Since the synthesis of air- and water-stable ionic liquids in 1992,[4] they have been widely explored as solvents and/or catalysts in synthetic chemistry. Welton[1] has reviewed many of these reaction studies in a recent paper. For example, catalytic hydrogenation of cyclohexene[5] using rhodium based homogeneous catalysts and hydrogenation of olefins[6] using ruthenium and cobalt based homogeneous catalysts in several ionic liquids showed enhancement in reaction rates and selectivity, compared to normal liquid solvents. In addition, very recent efforts have explored the separation of organic solutes from ILs with water[7] and with carbon dioxide,[8] as well as their use in the extraction of metal compounds such as strontium nitrate.[9]

A significant barrier to the use of ILs is the absence of understanding of how the structure of the IL affects its physical properties and solvent strength. Perhaps more importantly, there is a lack of understanding of how solvent strength and solvent polarity of various ILs affect reaction rates. Since polarity and polarizability are the simplest indicators of solvent strength, organic solvents are frequently classified on their ability to dissolve and stabilize dipolar or charged species. Fluorescent probes are commonly used to determine the solvent strength of organic solvents and recent studies indicate that these probes can be used to determine the solvent strength of ILs. For example, the solvent strength of alkylammonium thiocyanate organic salts was determined to be similar to cyclohexanone using fluorescent probes such as pyrene.[10] Bonhote *et al.* found that the solvent strength of 1-ethyl-3-methylimidazolium bis(triflyl)amide, using pyrene and pyrenecarbaldehyde, was similar to ethanol and hexane respectively, depending on the choice of the fluorescent probe.[11] In the present paper we report on the polarity of several ILs, (**I–IV**, Fig. 1) as measured by two fluorescent probes (**V** and **VI**).‡

While betaine dye (Reichardt's dye) is a common probe used to measure the polarity of homogeneous media,[12] neutral fluorescence probe molecules may be preferred when the large size and charge on the betaine dye is problematic. However, it is still quite common to express microscopic polarities in terms of the absorption energy of the betaine dye, $E_T(30)$. Another advantage with the fluorescent probes is that multiple solvent sensitive parameters, *e.g.* the location of the fluorescence maximum, the fluorescence quantum yield and the fluorescence lifetime, can be monitored. Taking this into consideration, we have chosen AP (**V**) and DAP (**VI**), fairly small, neutral molecules whose fluorescence properties are known to be highly sensitive to the polarity of the media[13–15] to explore the solvent strength of [bmim][$PF_6$], [$C_8$mim][$PF_6$], [bmim]$NO_3$] and [*N*-bupy][$BF_4$] (**I–IV**). The fluorescence properties of these probe molecules are shown in Table 1 in several protic and aprotic organic solvents. All three properties are very sensitive to the nature of the medium. The effect of the nature of the solvent on the fluorescence properties of these probes has been discussed in detail elsewhere.[12–14]

The frequency maxima, lifetimes and quantum yields of AP and DAP correlate reasonably well with the microscopic solvent polarity parameter, $E_T(30)$. For instance, the $\lambda_{max}$ of AP can be related to the $E_T(30)$ by $E_T(30)$ (kcal mol$^{-1}$) = 0.225 $\lambda_{max}$(nm) − 62.677 with a correlation coefficient of 0.94. We use these probes as general measures of the solvent strength of the various ILs shown in Fig. 1. As a result, we also report the equivalent $E_T(30)$ values determined from these correlations.[13,14]

The fluorescence properties of DAP were measured in four different ILs **I–IV**. The results are shown in Table 2, along with the equivalent $E_T(30)$ values estimated from the correlations that are obtained using the data given in Table 1. It is interesting to note that the solvent strength [as indicated by the equivalent $E_T(30)$ values] of the ILs, does not depend very strongly on which fluorophore is used, as demonstrated by the measurements in **I**. Moreover, the values do not depend strongly on what particular fluorescence parameter ($\lambda_{max}$, fluorescence lifetime or quantum yield) is used. These data provide more convincing estimates of the solvent strength than a single $E_T(30)$ measurement. Nonetheless, we did measure the $E_T(30)$ value of **I** using Reichardt's dye. A value of 55 kcal mol$^{-1}$ was obtained and this value compares reasonably well with the estimated values reported in Table 2.

All of the ILs exhibit solvent strengths as great or greater than the most polar aprotic solvent (acetonitrile) shown in Table 1. Clearly, these ILs are more polar than hexane, as has been suggested previously for some other ILs.[11] In fact, the equivalent $E_T(30)$ values for the ILs fall in the range of the various alcohols. The data presented in Table 2 suggest that both **I** and **III** provide more polar environments than those offered by

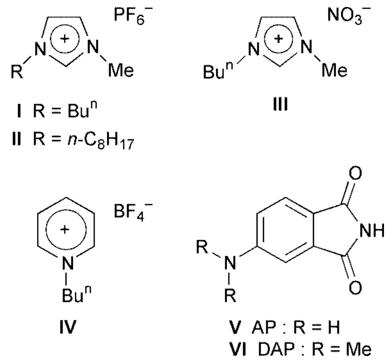

**Fig. 1** Structures of fluorescent probes and ionic liquids.

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**Table 1** Fluorescence properties of the probe molecules in selected organic solvents at room temperature[13,14]

| Solvent | Relative permittivity | $E_T(30)^{12}$/ kcal mol$^{-1}$ | AP[13,14] | | | DAP[13,14] | | |
|---|---|---|---|---|---|---|---|---|
| | | | $\lambda_{fluo}^{max}$/nm | $\phi_{fluo}$ | $\tau_{fluo}$/ns | $\lambda_{fluo}^{max}$/nm | $\phi_{fluo}$ | $\tau_{fluo}$/ns |
| Hexane | 1.887 | 31 | 416[a] | | | 437[a] | | |
| Diethyl ether | 4.2 | 34.5 | 425 | | | 440 | | |
| 1,4-Dioxane | 2.21 | 36 | 435 | 0.73 | 15.0 | 457 | 0.62 | 14.9 |
| Tetrahydrofuran | 7.58 | 37.4 | 445 | 0.7 | 12.4 | 459 | 0.52 | 13.8 |
| Acetone | 20.56 | 43.1 | 457 | 0.68 | | 483 | 0.17 | |
| Acetonitrile | 35.94 | 45.3 | 458 | 0.63 | 14.0 | 490 | 0.12 | 3.9 |
| *tert*-Butyl alcohol | 12.42 | 43.5 | 501 | | | 516 | | |
| Propan-2-ol | 19.92 | 48.5 | 505 | | | 523 | | |
| Ethanol | 25.3 | 51.9 | 509[a] | | | 523[a] | | |
| Methanol | 32.66 | 55 | 518 | 0.1 | | 534 | | |
| Water | 78.3 | 63.1 | 540 | 0.01 | | 562 | | |

[a] These values were estimated using the $E_T(30)$ values and the correlations developed.

**Table 2** Fluorescence properties of DAP in ILs at room temperature and the estimated $E_T(30)$ values (kcal mol$^{-1}$) in parentheses for the ILs[a]

| Solvent | DAP | | |
|---|---|---|---|
| | $\lambda_{fluo}^{max}$/nm | $\phi_{fluo}$ | $\tau_{fluo}$/ns |
| [bmim][$PF_6$] | 526 (52.39) | 0.028 (51.69) | 2.9 (46.16) |
| [$C_8$mim][$PF_6$] | 503 (46.84) | 0.18 (47.16) | 8.5 (41.51) |
| [bmim][$NO_3$] | 525 (52.14) | 0.045 (51.18) | |
| [*N*-bupy][$BF_4$] | 495 (44.91) | | 2.51 (46.48) |
| [bmim][$PF_6$] (dried) | 512 (49.01) | 0.036 (51.44) | |

[a] The steady state emission spectra were obtained in a 1 × 1 cmSuprasil quartz cell using a SLM-AMINCO 8100 spectrofluorometer. The fluorescence lifetime measurements were obtained with a PTI laserstrobe fluorescence spectrometer with excitation at 337 nm.

**II** and **IV**. In addition, we can conclude that replacing the counter ion, $PF_6^-$, by $NO_3^-$ does not change the apparent polarity of the medium. This may be caused by the fluorophore preferentially positioning itself near the imidazolium ring, thus not being significantly influenced by the anion. The fact that **I** is determined to be more polar than **II** is understandable, as an octyl group is expected to provide a more hydrophobic (hence non-polar) environment than the butyl substituent.

These ILs are expected to be at least partially miscible with water. In fact, measurements in our laboratory indicate that the equilibrium solubility of water in **I** at room temperature is *ca.* 1.735 M. In addition, the ILs are hygroscopic. In general, we would expect the probes used in the current work to be sensitive to the presence of water. To reduce the amount of water in the samples, they were dried *in vacuo* for at least 48 h at room temperature. Subsequent analysis by Karl–Fisher titration suggests that the water content is reduced to *ca.* 0.43 wt% (0.324 M) with this treatment. To further explore the effect of water on the measured $E_T(30)$ values, **I** was dried under even more stringent conditions, (*in vacuo* at 75 °C for 24 h), and Karl–Fisher analysis indicates that the water content should be down to 0.015 M. The fluorescence properties of DAP in this dried salt were measured and are shown at the bottom of Table 2. As expected, the fluorescence properties of the DAP in the dried sample did change somewhat, but the estimated $E_T(30)$ values indicate that the overall solvent strength of the sample is only reduced slightly from the previous measurements. Thus, we are confident that the solvent strengths of the ILs shown in Table 2 are faithful indications of their relative polarities.

In conclusion, the solvent strengths of **I**–**IV**, as represented by their equivalent $E_T(30)$ values, have been estimated using two fluorescent dyes. The results indicate that **I** is more polar than acetonitrile and less polar than methanol. The replacement of the counter ion, $PF_6^-$, by $NO_3^-$ did not change the apparent polarity of the medium. Also, both **I** and **III** provide more polar environments than those offered by **II** and **IV**. The presence of small amounts of water was found to have only a small effect on the estimated $E_T(30)$ values.

We appreciate the supply of samples of **II**, **III** and **IV** from the group of Professor Kenneth R. Seddon at the Queen's University of Belfast. In addition, financial support from the Environmental Protection Agency (R826734-01-0) and the National Science Foundation (EEC97-00537-CRCD) is gratefully acknowledged. The Notre Dame Radiation Laboratory is supported by the Division of Chemical Sciences of the U.S. Department of Energy. This is contribution No. NDRL 4254 from the Notre Dame Radiation Laboratory.

## Notes and references

‡ **I** was obtained from Sachem. The remaining ILs used in this work were prepared by the group of Professor Kenneth R. Seddon at the University of Belfast. All samples were dried *in vacuo* at room temperature for 24 h unless indicated otherwise in the text. The fluorescent probes were synthesized, as described elsewhere.[13,14]

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