Chemistry Letters Vol.33, No.11 (2004)

Polarity of Room-Temperature Ionic Liquid as Examined by EPR Spectroscopy

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(Received June 10, 2004; CL-040667)

Polarity of several ionic liquids was examined by ^{14}N hyperfine coupling constant of nitroxide radical measured by EPR method. Polarity judged from EPR agrees well with those by solvatochromic dyes, suggesting that EPR is another valuable probe for polarity of ionic liquids.

Air and water stable room-temperature ionic liquid (RTIL)[1] has been attracting much interest as a new type of solvent[2–4] with various properties such as high viscosity, low vapor pressure, and a wide electrochemical window. Potential of its application to chemistry is quite high. For example, RTIL can be a good electrolyte used under atmosphere. Nonvolatile nature is also important in industrial synthetic processes because usage of RTILs may reduce emission of solvent to atmospheric environment.[5]

In a choice of solvent, we usually examine a solvent polarity. For evaluation of a polarity, there are several methods such as electronic absorption measurement of solvatochromic dyes, the chemical shift of ^{19}F NMR in fluorinated compounds and the isotropic hyperfine EPR coupling constants of ^{14}N (a_N) of nitroxide radicals.[6] For a polarity of RTIL, there are recent publications using solvatochromic dye probes,[7–11] and empirical polarity values such as $E_T(30)$ values were determined to discuss solvation in RTILs. Although the method using dyes is simple and conventional, one needs to care the contribution of both solvation in S_0 and S_1 states. Meanwhile, EPR spectroscopy for a_N value is another simple method and only the solvation in the ground state of nitroxide is concerned.[12,13] Therefore, it is worthwhile to examine polarity of RTILs by an EPR method and to demonstrate both methods of EPR and solvatochromic dyes are available for RTILs. Besides, it is known that EPR spectroscopy of nitroxide is a tool to probe tumbling motion in usual liquids[14] and it may be easy to determine rotation correlation times, τ_r of nitroxide in RTILs from line shape analysis. We discuss the microscopic solvation in RTILs according to the results of EPR measurements.

The inset of Figure 1 shows EPR spectrum of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (ATEMPO) radical observed in a widely examined RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]), solution. A triplet hyperfine structure due to a nitrogen atom shows nonequal intensity pattern, which suggests a restricted tumbling motion of ATEMPO. An a_N value of 16.30 G was determined by averaging the high- and low-field hyperfine lines. The similar measurements were carried out for several RTILs and the a_N values are summarized in Table 1. For comparison, a_N values in molecular solvents are also summarized. The a_N values of RTILs range from 16.02 to 16.32 G. These values are relatively large and are close to those in ethanol and in ethylene glycol. The a_N value of ATEMPO is controlled by the charge-transfer (CT) nature of the N–O group. Polar solvent stabilizes the CT canonical structure as illustrated in Scheme 1a and the electron spin density at N atom is enhanced, which results in a larger a_N value in polar solvent.[13,14] A hydrogen at C2 in bmim$^+$ involves in hydrogen-bonding (H-bonding) with anion as pointed out by an NMR study[16] and the resultant H-bond should be formed at an O atom in ATEMPO shown in Scheme 1b. The similar picture is expected for H-bond formation in RTILs with NR$_4$ cation. The a_N values of RTILs with NR$_4$ are 16.02 G, while those with bmim and emim are about 16.3 G. This observation seems to suggest that the a_N value is primarily controlled by a cation component of

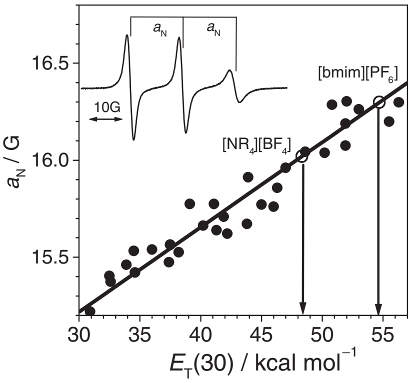
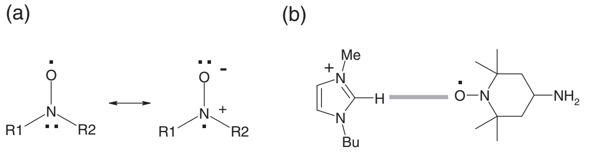


Figure 1. A plot of a_N vs $E_T(30)$ values. Data for closed circles are from ref. 13. Inset is an EPR spectrum of ATEMPO (6×10^{-4} mol dm^{-3}) in [bmim][PF$_6$] ionic liquid at 293 K.

Table 1. Properties of ATEMPO in RTILs and molecular solvents determined by EPR and estimated $E_T(30)$ values

Solvents[a]	a_N/G	$E_T(30)$ /kcal mol^{-1}	τ_r/ns
[bmim][PF$_6$]	16.30	54.8[b]	0.94
[bmim][BF$_4$]	16.26	53.9[b]	1.4
[(bmim)$_2$][WO$_4$]	16.07	49.6[b]	1.7
[emim][CF$_3$SO$_3$]	16.32	55.3[b]	0.83
[NR$_4$][BF$_4$]	16.02	48.4[b]	0.54
[NR$_4$][N(SO$_2$CF$_3$)$_2$]	16.02	48.4[b]	0.46
Mineral oil	15.2[c]	—	0.13[c]
Benzene	15.53[d]	34.5[d]	0.02
Acetonitrile	15.76[d]	46.0[d]	—
Ethanol	16.08[d]	51.9[d]	0.05
Ethylene glycol	16.30[d]	56.3[d]	—
Water	16.99[d]	63.1[d]	—

[a]Abbreviations are emim: 1-ethyl-3-methylimidazolium, and NR$_4$: 2-methoxyethyldiethylmethylammonium. [b]Estimated by a_N. [c]Ref. 15. [d]Ref. 13.



Scheme 1. (a) Two canonical structures of nitroxide and (b) a hydrogen-bonded structure of ATEMPO dissolved in [bmim][PF_6].

RTILs and probably the anion contribution is small. This agrees well with the H-bonding mechanism described above. The a_N values in RTILs with NR_4 are smaller than those in RTILs with imidazolium and the H atom in NR_4 seems to form weaker H-bond. The g value of ATEMPO decreases from 2.0062 in mineral oil, a nonpolar molecular solvent, to 2.0057 in [bmim][PF_6]. This reduction of g value is also indicative of H-bond effect in [bmim][PF_6].

The $E_T(30)$ is widely quoted empirical parameter for polarity[6] and the values have been reported for many RTILs recently. To investigate the correlation between $E_T(30)$ and a_N values for RTILs, we tried to estimate $E_T(30)$ values of the RTILs from the a_N values as follows. A good correlation between a_N and $E_T(30)$ values[13] is demonstrated in Figure 1 where closed circles represent a plot of a_N vs $E_T(30)$ values for various molecular solvents reported previously. Although the plot slightly scatters, the correlation between a_N and $E_T(30)$ values seems good enough to estimate an unknown $E_T(30)$ value from a known a_N value. For example, two a_N values in [bmim][PF_6] and in [NR_4][BF_4] are plotted as two open circles on a best-fitted straight line, $a_N = 0.0438\,\mathrm{G}\ (\mathrm{kcal\,mol^{-1}})^{-1} \times E_T(30) + 13.901\,\mathrm{G}$ in Figure 1 and the corresponding $E_T(30)$ values are estimated from horizontal axis. These $E_T(30)$ values are also summarized in Table 1. Reported values[7] of $E_T(30)$ for [bmim][PF_6] are 52.4–54 $\mathrm{kcal\,mol^{-1}}$, which are close to 54.8 $\mathrm{kcal\,mol^{-1}}$ by EPR method. The $E_T(30)$ values of RTILs with NR_4 are relatively small as 48.4 $\mathrm{kcal\,mol^{-1}}$. This value accords with the literature[9] reporting that the $E_T(30)$ values of tetraalkylammonium ionic liquids are 45.5–50.9 $\mathrm{kcal\,mol^{-1}}$. Since the estimated $E_T(30)$ values agree with those determined by the optical spectrometry of solvatochromic dyes, we conclude that the a_N value of ATEMPO can be used as another polarity probe of RTILs. Empirical value of polarity should include uncertainty due to specific solvent-probe interactions. Scatter in the plot of $E_T(30)$ and a_N values is a good example showing this nature. Polarity may depend on the solute of interest and a choice of probe for one's purpose is important.

The EPR line shape reflects the spin relaxation process due to a tumbling motion of ATEMPO.[14] Previously, ionic liquids of [$(\mathrm{bmim})_n$][$(\mathrm{AlCl_4})_m$] were studied by EPR and the τ_r of ATEMPO was examined.[15] We applied this method to determine the τ_r in RTILs and the results are given in Table 1. The values of 0.46–1.7 ns are much larger than those in ethanol and in benzene. One prominent character of RTILs is high viscosity (>50 cP) at ambient temperature[17] and it is reasonable that τ_r is longer in RTILs. Moreover, there may be an additional friction between ATEMPO and solvents. For instance, viscosity[8] of [bmim][PF_6] is ca. 286 cP at 293 K which is close to 264 cP of mineral oil with τ_r of 0.13 ns.[15] This τ_r value is much smaller than that in [bmim][PF_6], which suggests the tumbling motion is hindered in RTILs. This may be due to H-bond between the cation and ATEMPO.

ATEMPO presents an intense EPR signal and the concentration of $10^{-5}\ \mathrm{mol\,dm^{-3}}$ was found to be high enough for EPR measurements. ATEMPO is commercially available and physically stable free radical. It is clear from these points that the a_N value measured by EPR is valuable to examine the polarity of RTILs. In particular, when a solvent itself has a strong UV–vis absorption, which prevents us from measuring the electronic spectra of dye molecules, the EPR method can be employed as the most appropriate probe. This advantage is based on EPR principle that the EPR spectrum is not sensitive to UV–vis chromphors unless they are paramagnetic. RTIL is called as 'designers solvent' since the solvent properties are designed by a combination of anion and cation.[2] There are possibilities that RTIL with strong absorption in a UV–vis wavelength region are valuable for some purpose. For evaluation of the polarity of these RTILs, we believe that the EPR spectrometry would serve as a powerful tool.

We appreciate Professor T. Kitazume and his group for providing us RTIL samples and for stimulating discussion. [bmim][PF_6] was prepared in our group by the method in Ref. 4. EPR spectra were measured by one of on-campus cooperative research facilities in Tokyo Institute of Technology, "a pulsed ESR system (Bruker E-580)." This work is partly supported by Grant-in-Aid for Scientific Research (No. 15550005 and 13127202) from the Ministry of Education, Culture, Sports Science and Technology, Japan.

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Published on the web (Advance View) October 9, 2004; DOI 10.1246/cl.2004.1464