Polarity Measurement for Ionic Liquids Containing Dissociable Protons

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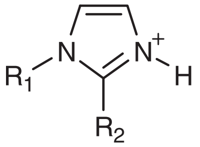
Polarity of a series of ionic liquids (ILs) prepared by neutralization of *N*-alkylimidazoles and acids was measured with solvatochromic dye, Nile Red. Polarity of the *N*-alkylimidazolium salt-type ILs was in the comparable range to that of *N*,*N*′-dialkylimidazolium salt-type ILs. In the range, higher polarity was found when stronger acid (small pK_a value in water) was used. This is the first report on the polarity of ILs containing dissociable protons.

ILs have been vigorously investigated owing to their unique characteristics to apply reaction solvents[1] or ion conductive materials.[2] Most of ILs are composed for quaternary onium cations, for example *N*,*N*′-dialkylimidazoliums, *N*-alkylpyridiniums, and so on.[3] On the other hand, ILs could also be obtained by neutralization of tertiary amines with acids.[4] In this article, we call them protic ILs (Ionic liquids containing dissociable proton)[5] in order to distinguish them with quaternary onium salt-type ILs. This neutralization process provides a wide variety of protic ILs by enormous combination of acids and bases without any by-product. Thus obtained protic ILs are useful as model compounds for corresponding quaternary onium type ILs. In addition these protic ILs are expected to show proton conductive properties.[6]

Since the correlation between structure and property of ILs is important to design the ILs having required properties, characterization is the first priority requirement in this field. Physicochemical properties such as melting point, viscosity, potential windows and ionic conductivity have already been measured. However, some properties of ILs such as polarity or solubility in organic or inorganic have insufficiently been investigated. Because dielectric measurement for ILs cannot be used for polarity measurements owing to ion conductive nature, solvatochromism of dye molecules has been alternatively used.[7] Polarity measurements of protic ILs were hardly carried out, except for aliphatic amine-based protic ILs.[8] As has been previously described, the ILs containing active proton recently attracted keen attention owing to showing specific functions such as catalytic activity[9] or proton conductivity.[6] There are increasing needs to measure polarity of the ILs having highly dissociable protons including protic ILs. In this work, we found suitable solvatochromic dye to measure the polarity of protic ILs, and we studied correlation between polarity and structure of component ions.

The protic ILs were prepared by the neutralization method according to the reported.[4] Obtained salts were dried under reduced pressure at 80 °C for one day. Only a series of *N*-alkylimidazolium carboxylates were prepared by mixing of imidazole derivatives with equimolar carboxylic acids in the bulk without any purification. The structure of the obtained ILs was confirmed with ^{1}H NMR spectroscopy. Water content of each ILs was determined below 0.5 wt % by using Karl–Fischer titration (MKC-510N; Kyoto Electronics Co., Ltd.). Structure of imidazolium cation used in the present study is shown in Scheme 1.



1: R_1 = Me, R_2 = H
2: R_1 = Et, R_2 = H
3: R_1 = Bu, R_2 = H
4: R_1 = Me, R_2 = Me
5: R_1 = Et, R_2 = Me
6: R_1 = Pr, R_2 = Me
7: R_1 = i-Bu, R_2 = Me

Scheme 1. Structure of imidazolium cation analyzed.

The Reichardt dye[10] is a famous solvatochromic dye for not only organic solvents but also several ILs. From our preliminary experiments, the Reichardt dye was confirmed not to be applicable to the polarity measurement of protic ILs. The proton on the nitrogen atom to form quaternary onium cation jumped into phenoxide moiety of the Reichardt dye due to weaker basicity of *N*-alkylimidazoles than that of the Reichardt dye. In order to measure the polarity of protic ILs, it is requested to use other solvatochromic dyes that keep intramolecular charge transfer even in an acidic condition and show the maximum absorption. We chose three solvatochromic dyes such as 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate, 1-ethyl-4-methoxycarbonylpyridinium iodide, and Nile Red according to those requirements. Each dye was dissolved in ILs in the concentration range of 10^{-5} to 10^{-4} M. Absorption spectra of dyes were recorded on a Shimadzu UV–vis spectrophotometer UV-2500PC. IL solutions were examined in quartz cuvette with 1-mm light path length or thin layer glass cells with 0.1-mm light path length. Dyes, except for Nile Red dissolved in protic ILs, showed no characteristic maximum absorption in appropriate visible region. The fact pushed us to evaluate Nile Red as a solvatochromic dye to estimate polarity of the protic ILs.

Table 1 shows the maximum absorption and molar transition energy (E_{NR}), which was calculated from the maximum absorption for Nile Red dissolved in BF_4 salts. The polarity of these

Table 1. Spectroscopic data of Nile Red and the calculated polarity for *N*-alkylimidazolium tetrafluoroborate (BF_4) and starting amine at 25 °C

Cation[a]	BF_4 Salt λ_{max} / nm (E_{NR} / kcal mol^{-1})	Starting Amine λ_{max} / nm (E_{NR} / kcal mol^{-1})
5	565.4 (50.6)	546.8 (52.3)
6	564.4 (50.7)	545.1 (52.5)
2	562.9 (50.8)	551.1 (51.9)
3	562.8 (50.8)	547.1 (52.3)
7	562.5 (50.8)	544.0 (52.6)
1	562.3 (50.9)	549.6 (52.0)
4	s	547.3 (52.2)

$E_{NR} = (hcN_A/\lambda_{max})$, *s*: solid state at room temperature.
[a]See Scheme 1.

protic ILs was higher than that of ILs based on corresponding N,N'-dialkylimidazolium cation. The E_{NR} in protic ILs was approximately the same value regardless of substituent. It is known that the polarity of N,N'-dialkylimidazolium salt is lowered by substituting the proton on 2-position on imidazole ring with methyl group[11] because of the acidic proton. In the case of protic ILs, dissociable proton at 3-position might be also effective to raise the polarity as well as the proton at 2-position.

Table 2. Spectroscopic data and calculated polarity obtained with Nile Red in several *N*-ethylimidazolium salt-type protic ILs

Anion species	λ_{max} / nm (E_{NR} / kcal mol^{-1})	pK_a of acid (in water as it is)[13]	Anion Radius / nm[14]
BETI	573.1 (49.9)	[a]	
TFSI	566.4 (50.5)	[a]	0.325
BF_4	562.9 (50.8)	0.5	0.299
$BzSO_3$	560.1 (51.1)	0.7	
CF_3SO_3	557.3 (51.3)		0.27
NO_3	555.7 (51.5)	−1.64	0.189
CH_3SO_3	551.8 (51.8)	−2.6	
$CH_3CH_2SO_3$	551.1 (51.9)		
$CH_3(CH_2)_2SO_3$	548.2 (52.1)		
CF_3CO_2	545.1 (52.5)	−0.3	
HCO_2	552.4 (51.8)	3.75	
CH_3CO_2	547.5 (52.2)	4.76	0.162
$CH_3CH_2CO_2$	548.0 (52.2)	4.87	
$CH_3(CH_2)_2CO_2$	546.5 (52.3)	4.83	

[a] Strong acid without published pK_a in water.[12]

Table 2 shows the E_{NR} of *N*-ethylimidazolium salt with several different anions, their dissociation constants (pK_a) and anion radii. In the table, BETI and TFSI implied bis(perfluoroethylsulfonyl)imide anion and bis(trifluoromethylsulfonyl)imide anion. The maximum absorption changed significantly depended on counter anion species in contrast to the case varying imidazolium cation structure as shown in Table 1. The polarity of protic ILs composed of strong acids (small pK_a) tended to be high. Generally, higher polarity was found for those with larger anions. However the polarity of protic ILs is not the function of only pK_a or anion size. Negative charge delocalization and other factors might intricately concern the polarity.

Water content changes viscosity and ionic conductivity of ILs. In order to investigate the effect of water content on the polarity of protic ILs, we measured the polarity of *N*-ethylimidazolium tetrafluoroborate with different water content. The maximum absorption of Nile Red was 562.9 nm (50.8 kcal mol^{-1}) when the salt containing 0.27 wt % water, 564.7 nm (50.6 kcal mol^{-1}) for 2.5 wt %, and 570.7 nm (50.1 kcal mol^{-1}) for 21 wt %. We found certain effect of water on the polarity of protic ILs. However, it is not so significant compared to the effect of anion species as reported for some ILs.[15]

In conclusion, Nile Red was confirmed to be suitable as solvatochromic probe for the protic ILs prepared by the neutralization method, and their polarity depended on ion species.

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