

Solvent Polarities and Kamlet–Taft Parameters for Ionic Liquids Containing a Pyridinium Cation

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Five recently synthesized pyridinium ionic liquids [(1-butyl-4-methylpyridinium, 1-octylpyridinium, 1-octyl-2-methylpyridinium, 1-octyl-3-methylpyridinium, and 1-octyl-4-methylpyridinium, all with anion bis(trifluoromethylsulfonyl)imide], were investigated to establish the influence of substituting a methyl group and the influence of alkyl chain length on the cation on polarity E_T^N and on three Kamlet–Taft parameters: dipolarity/polarizability (π^*), hydrogen-bond acidity (α), and hydrogen-bond basicity (β). Experimental measurements cover the range 25 to 65 °C.

Introduction

In recent years, much attention has been given to room-temperature ionic liquids because such liquids may have significant advantages relative to conventional organic solvents for separation processes^{1–4} and as media for chemical and biochemical reactions.^{5–10} Most ionic liquids are stable at high temperatures and have essentially zero vapor pressure at ordinary temperatures.

To facilitate selection of an optimum ionic liquid for a particular application, it is useful to consider some fundamental properties of ionic liquids. Toward that end, we have obtained polarities and Kamlet–Taft parameters for five ionic liquids. Our results indicate how some solvent characterizing properties of ionic liquids are related to their molecular structure.

Most published work has focused on ionic liquids containing imidazolium cations. The polarity of [EMIM]⁺[(CF₃SO₂)₂N][−] and that of [BMIM]⁺[(CF₃SO₂)₂N][−] are close to that of 2-butanol but slightly less than those for imidazolium ionic liquids containing tetrafluoroborate anions.^{11–13}

In this work, we report results for five recently synthesized pyridinium ionic liquids.¹⁴ Our spectroscopic measurements were made with three dyes: Reichardt's dye, *N,N*-diethyl-4-nitroaniline, and 4-nitroaniline.

Experimental Section

As reported earlier,¹⁴ we have synthesized five new ionic liquids: 1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4MBPYR]⁺[Tf₂N][−]), 1-octylpyridinium bis(trifluoromethylsulfonyl)imide ([OPYR]⁺[Tf₂N][−]), 1-octyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide ([2MOPYR]⁺[Tf₂N][−]), 1-octyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide ([3MOPYR]⁺[Tf₂N][−]), and 1-octyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4MOPYR]⁺[Tf₂N][−]).

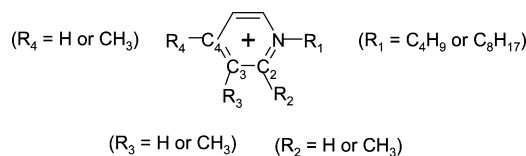


Figure 1. Structures of pyridinium cations in ionic liquids.

Figure 1 shows the structures of pyridinium cations for five ionic liquids, and Table 1 identifies abbreviations.

All ionic liquids were dried under vacuum for 7 days and stored in a dry box. The water content of each ionic liquid was no more than 50 ppm.¹⁵ 4-Nitroaniline and 2,6-diphenyl-4-(2,4,6-triphenylpyridio)phenolate (Reichardt's dye) were used as received from Sigma. *N,N*-Diethyl-4-nitroaniline was used as received from Frinton Laboratory.

In a dry box, a dye was dissolved in an ionic liquid in the concentration range 10^{-5} to 10^{-4} M. A sample was loaded into a dry cuvette. The cuvette was capped and sealed in a dry box. As described previously,¹⁶ the dye was not aggregated. Absorbance was measured with a Cary-400-Bio UV–visible spectrophotometer. Temperature was controlled by a Cary 1 × 1 Peltier temperature controller (± 0.1 °C). Each absorbed peak was fit with a Gaussian profile to obtain the wavelength corresponding to its maximum value. To test our procedure, we made measurements for [HMIM]⁺[Tf₂N][−] and [BMIM]⁺[PF₆][−]; at 25 °C, our measured polarities of [HMIM]⁺[Tf₂N][−] and [BMIM]⁺[PF₆][−] agree within 1% with those in the literature.¹⁷ Estimates of errors reported in Tables 2–7 and plotted in Figures 2–5 are within 1%.

Data Reduction

A zwitterion compound, known as Reichardt's dye, has been widely used to determine the polarity of a solvent. One of the most widely used scales for polarity is the E_T scale that is determined by the charge-transfer absorption band of the dye in a solvent. E_T (30), where 30 indicates the number assigned to this dye, represents the energy required to go to the excited-state from the ground state. The E_T (30) and E_T^N scales express solvent polarity arising from overall interactions between a solvent and the dye. In a sense, therefore, the E_T^N solvent scale

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TABLE 1: Abbreviations for Five Ionic Liquids Studied Here

abbreviation	full name
[4MBPYR] ⁺ [Tf ₂ N] ⁻	1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide
[OPYR] ⁺ [Tf ₂ N] ⁻	1-octylpyridinium bis(trifluoromethylsulfonyl)imide
[2MOPYR] ⁺ [Tf ₂ N] ⁻	1-octyl-2-methylpyridinium bis(trifluoromethylsulfonyl)imide
[3MOPYR] ⁺ [Tf ₂ N] ⁻	1-octyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide
[4MOPYR] ⁺ [Tf ₂ N] ⁻	1-octyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide

TABLE 2: E_T^N and Kamlet–Taft Parameters for Five Ionic Liquids at 25 °C. For Comparison, Results Are Also Shown for a Few Imidazolium Ionic Liquids and for a Few Common Solvents

liquid	E_T^N	α	β	π^*
[4MBPYR] ⁺ [Tf ₂ N] ⁻	0.588	0.51	0.29	0.98
[OPYR] ⁺ [Tf ₂ N] ⁻	0.588	0.51	0.28	0.99
[2MOPYR] ⁺ [Tf ₂ N] ⁻	0.554	0.48	0.35	0.95
[3MOPYR] ⁺ [Tf ₂ N] ⁻	0.576	0.50	0.33	0.97
[4MOPYR] ⁺ [Tf ₂ N] ⁻	0.576	0.50	0.33	0.97
[BMIM] ⁺ [Tf ₂ N] ⁻ (¹⁷)	0.642			
[OMIM] ⁺ [Tf ₂ N] ⁻ (¹⁷)	0.630			
[BMIM] ⁺ [PF ₆] ⁻ (²⁰)	0.669	0.634	0.207	1.032
[BMIM] ⁺ [TfO] ⁻ (²⁰)	0.656	0.625	0.464	1.006
[BMIM] ⁺ [N(Tf) ₂] ⁻ (²⁰)	0.644	0.617	0.243	0.984
[BMPY] ⁺ [N(Tf) ₂] ⁻ (²⁰)	0.544	0.427	0.252	0.954
Water(²²)	1.000	1.12	0.14	1.33
methanol(²²)	0.762	1.05	0.61	0.73
acetone(²²)	0.35	0.20	0.54	0.70
dichloromethane(²²)	0.31	0.04	-0.01	0.79
hexane(¹²)	0.009	0.07	0.04	-0.12

used here summarizes our solvent-property studies. The normalized E_T^N polarity is obtained by measuring the wavelength corresponding to maximum absorption¹⁸ in a solvent:

$$E_T^N = \frac{E_T(30) - 30.7}{32.4} \quad (1)$$

where $E_T(30)$ in kcal·mol⁻¹ is 28591/ λ_{\max} (nm); here, λ_{\max} is the wavelength corresponding to maximum absorption.

Kamlet–Taft parameter π^* is obtained by measuring the wavelength of maximum absorbance, ν_{\max} in kK (kilokeyser, 10⁻³ cm⁻¹), of the dye *N,N*-diethyl-4-nitroaniline:¹⁹

$$\pi^* = \frac{\nu_{\max} - \nu_0}{s} \quad (2)$$

where $\nu_0 = 27.52$ kK and $s = -3.182$; here, ν_0 is the regression value for a reference solvent system and s is the susceptibility of intensity of spectral absorption due to changing solvent dipolarity/polarizability. Parameter π^* provides a measure of a solvent's dipolarity/polarizability ratio.

Kamlet–Taft parameter α was determined by:¹⁹

$$\alpha = \frac{(E_T(30) - 14.6(\pi^* - 0.23) - 30.31)}{16.5} \quad (3)$$

Parameter α provides a measure of a solvent's hydrogen-bond-donating acidity (HBD).

Kamlet–Taft parameter β was obtained by measuring the relative difference of solvatochromism between 4-nitroaniline (1) and *N,N*-diethyl-4-nitroaniline (2):¹⁹

$$\beta = \frac{(1.035\nu(2)_{\max} - \nu(1)_{\max} + 2.64)}{2.8} \quad (4)$$

where $\nu(1)_{\max}$ and $\nu(2)_{\max}$ are the wavelengths of maximum absorbance of dissolved 4-nitroaniline and *N,N*-diethyl-4-

TABLE 3: E_T^N and Kamlet–Taft Parameters as a Function of Temperature for [4MBPYR]⁺[Tf₂N]⁻

temp (°C)	E_T^N	α	β	π^*
25	0.588	0.51	0.29	0.98
35	0.585	0.53	0.30	0.96
45	0.583	0.55	0.32	0.93
55	0.581	0.58	0.34	0.90
65	0.574	0.58	0.33	0.88

TABLE 4: E_T^N and Kamlet–Taft Parameters as a Function of Temperature for [OPYR]⁺[Tf₂N]⁻

temp (°C)	E_T^N	α	β	π^*
25	0.588	0.51	0.28	0.99
35	0.585	0.51	0.31	0.98
45	0.583	0.52	0.28	0.97
55	0.577	0.52	0.30	0.95
65	0.570	0.53	0.29	0.93

TABLE 5: E_T^N and Kamlet–Taft Parameters as a Function of Temperature for [2MOPYR]⁺[Tf₂N]⁻

temp (°C)	E_T^N	α	β	π^*
25	0.554	0.48	0.35	0.95
35	0.551	0.51	0.40	0.90
45	0.550	0.53	0.39	0.89
55	0.549	0.53	0.40	0.88
65	0.548	0.53	0.38	0.88

TABLE 6: E_T^N and Kamlet–Taft Parameters as a Function of Temperature for [3MOPYR]⁺[Tf₂N]⁻

temp (°C)	E_T^N	α	β	π^*
25	0.576	0.50	0.33	0.97
35	0.572	0.51	0.32	0.95
45	0.570	0.53	0.35	0.93
55	0.561	0.53	0.37	0.91
65	0.548	0.53	0.38	0.88

TABLE 7: E_T^N and Kamlet–Taft Parameters as a Function of Temperature for [4MOPYR]⁺[Tf₂N]⁻

temp (°C)	E_T^N	α	β	π^*
25	0.576	0.50	0.33	0.97
35	0.569	0.51	0.32	0.95
45	0.566	0.52	0.35	0.93
55	0.551	0.51	0.37	0.90
65	0.549	0.54	0.39	0.87

nitroaniline, respectively. Parameter β provides a measure of a solvent's hydrogen-bond-accepting basicity (HBA).

Table 2 shows E_T^N and Kamlet–Taft parameters at 25 °C for five pyridinium ionic liquids. Tables 3–7 provide detailed results. Figure 2 shows E_T^N polarities for five ionic liquids as a function of temperature.

At 25 °C, the polarities of our five ionic liquids are higher than those of acetone, dimethylformamide, dimethyl sulfoxide, cyclohexanol, and a pyrrolidinium ionic liquid; however, they are slightly lower than those of imidazolium ionic liquids.^{19,20} Compared to the polarities for pyridinium and imidazolium ionic liquids, the symmetric head structure of a pyridinium cation shows a lower polarity than that for the unsymmetric head structure of an imidazolium cation. Polarities of [4MBPYR]⁺[Tf₂N]⁻ and [OPYR]⁺[Tf₂N]⁻ are the highest. The polarity of [4MOPYR]⁺

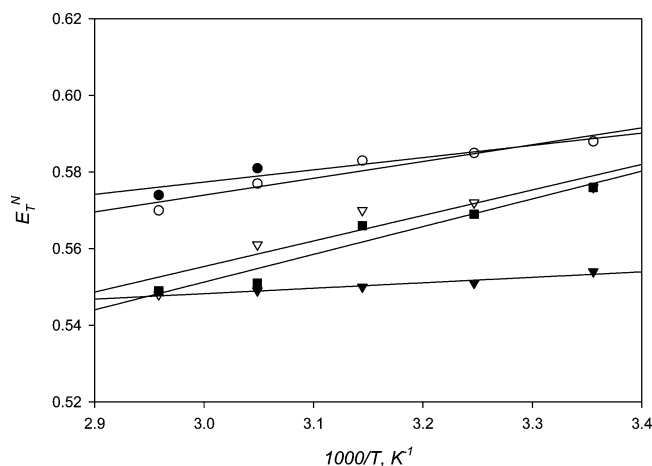


Figure 2. E_T^N polarities for five ionic liquids as a function of temperature for the range 25 to 65 °C. [4MBPYR]⁺[Tf₂N][−] (●), [OPYR]⁺[Tf₂N][−] (○), [2MOPYR]⁺[Tf₂N][−] (▼), [3MOPYR]⁺[Tf₂N][−] (□), and [4MOPYR]⁺[Tf₂N][−] (■).

[Tf₂N][−] is slightly lower than that of [4MBPYR]⁺[Tf₂N][−], indicating that an increase of alkyl-chain length on the pyridinium cation produces a small decrease in polarity, in agreement with previous results for imidazolium ionic liquids and primary alcohols.^{17,20}

Addition of a methyl group on the 1-octylpyridinium cation causes a decrease in E_T^N . The polarity of [2MOPYR]⁺[Tf₂N][−] is lower than those for [3MOPYR]⁺[Tf₂N][−] and [4MOPYR]⁺[Tf₂N][−], indicating that the hydrogen interaction between the phenoxide group on the dye and a hydrogen atom in the C(2) position is stronger than those in the C(3) or C(4) position on the 1-octylpyridinium cation. Thus, substituting a methyl group in the C(2) position on the cation reduces hydrogen-bond contributions on the E_T^N scale; this substitution reduces hydrogen bond-donor ability. Hydrogen-bond contributions of imidazolium ionic liquids have been reported using crystallographic data.²¹

As expected, the polarities of the ionic liquids decrease with rising temperature due to negative solvatochromism; with increasing solvent polarity, the dipolar ground-state is more stabilized by solvation than the less dipolar Franck–Condon excited state.¹⁸ Linear behavior of polarity as a function of reciprocal temperature is reported for [BMIM]⁺[PF₆][−] by Baker et al., suggesting monotonic changes in the capability of hydrogen-bond donor of [BMIM]⁺[PF₆][−] with temperature.¹⁶ The linear behavior may be related to a monotonic decrease in hydrogen-bond donor capability of an ionic liquid as well as to a decrease in interaction or favorable orientation among charged species: dye, cation, and anion, as temperature rises. The effect of temperature on the polarity of [2MOPYR]⁺[Tf₂N][−] is small when compared with that for other ionic liquids.

Figure 3 shows parameter π^* for five ionic liquids. At 25 °C, they are higher than those for methanol, 2-butanone, and nitromethane and are close to those for dichloromethane and for imidazolium ionic liquids.^{17,20} The effect of solvation of the dye by a solvent on its ground state and on its electron-excited-state depends not only on the solvent dipolarity relative to polarizability but also on solvent–dye interactions.¹⁸ Parameter π^* for [2MOPYR]⁺[Tf₂N][−] is lower than those for the other ionic liquids. A decrease in π^* , by substituting a methyl group in the C(2) position on 1-octylpyridinium cation, may be due to the decrease of Coulombic interactions from delocalization of charge on the cation relative to the delocalization of charge on the anion with *N,N*-diethyl-4-nitroaniline. As temperature rises, π^* decreases due to negative solvatochromism.

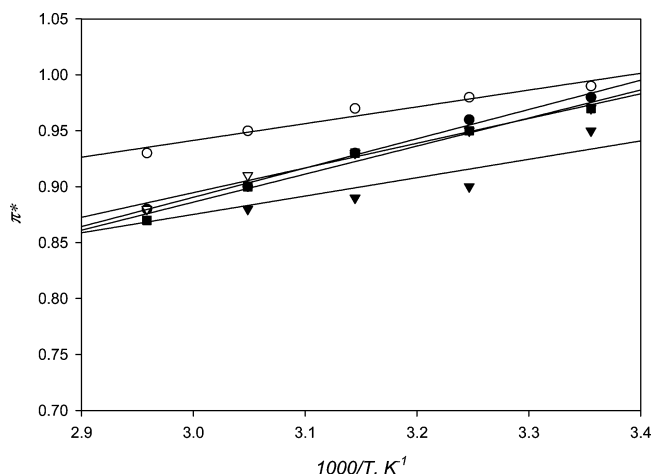


Figure 3. Parameter π^* for five ionic liquids as a function of temperature for the range 25 to 65 °C. Symbols as in Figure 2.

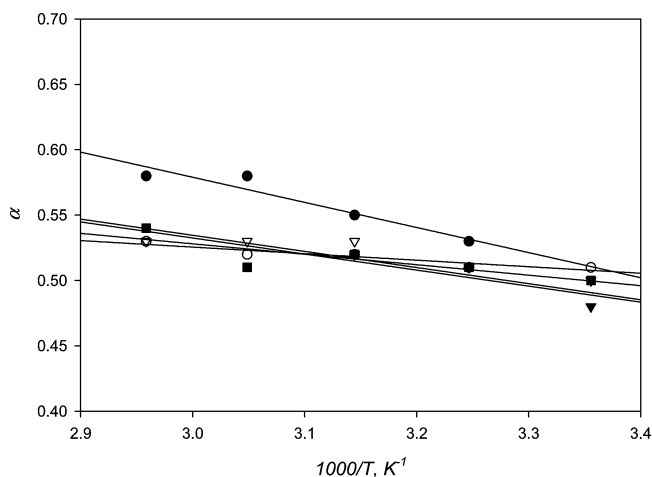


Figure 4. Parameter α for five ionic liquids scale as a function of temperature for the range 25 to 65 °C. Symbols as in Figure 2.

The π^* parameter for [OPYR]⁺[Tf₂N][−] is higher than those for the other pyridinium ionic liquids. For parameter π^* , the effect of alkyl-chain length on the cation is negligible when compared with results for [4MBPYR]⁺[Tf₂N][−] and [4MOPYR]⁺[Tf₂N][−]. The effect on π^* upon substituting a methyl group in the C(3) or C(4) position on the 1-octylpyridinium cation is relatively small when compared to that of substituting a methyl group in the C(2) position. However, substitution of a methyl group on the cation lowers π^* when temperature rises.

Figure 4 shows parameter α as a function of temperature. For the pyridinium ionic liquids at 25 °C, α parameters are higher than those for acetonitrile and acetone; they are slightly lower than those for imidazolium ionic liquids but higher than that for an pyrrolidinium ionic liquid.^{17,20} At 25 °C, parameter α for [2MOPYR]⁺[Tf₂N][−] is lower than those for the others, indicating that a C(2)-H hydrogen atom on the 1-octylpyridinium cation is less acidic than a hydrogen atom in the C(3) or C(4) position, consistent with our results for polarity. The effect of a weak acidic hydrogen atom is more pronounced in heterocyclic imidazolium ionic liquids when a methyl group is substituted in the C(2) position between alkyl groups on C(1) and C(3). However, this effect becomes negligible as temperature increases.

As temperature rises, parameter α for [4MBPYR]⁺[Tf₂N][−] is higher than those for the others, indicating that when temperature rises, the capability of hydrogen-bond-donating

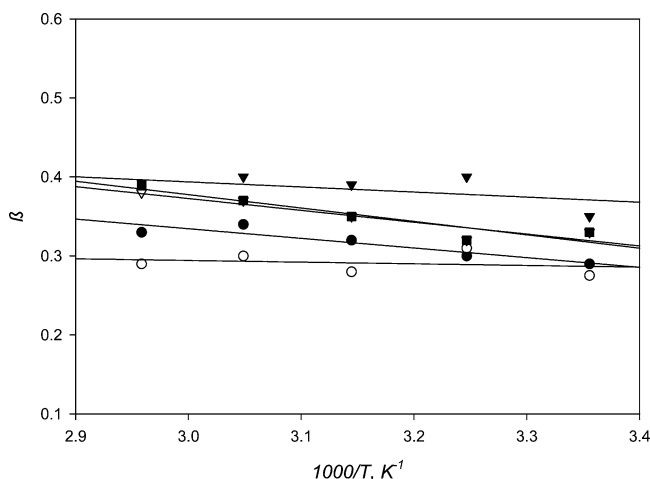


Figure 5. Parameter β for five ionic liquids as a function of temperature for the range 25 to 65 °C. Symbols as in Figure 2.

acidity of the pyridinium cation depends on the length of the alkyl chain rather than on the position of a methyl group.

Figure 5 shows parameter β as a function of temperature. At 25 °C, β parameters for our ionic liquids are close to those for acetonitrile and for imidazolium ionic liquids, and to that for a pyrrolidinium ionic liquid.²⁰ Unlike α , for imidazolium ionic liquids, β depends on the nature of the anion. Because anion ($[\text{Tf}_2\text{N}]^-$) is fixed in our studies, the β parameters for our ionic liquids do not vary significantly. Nevertheless, we observe that a methyl group on the pyridinium influences parameter β . At 25 °C, parameter β for $[\text{2MOPYR}]^+[\text{Tf}_2\text{N}]^-$ is higher than those for the others. Parameter β is lowest for $[\text{OPYR}]^+[\text{Tf}_2\text{N}]^-$ and $[\text{4MBPYR}]^+[\text{Tf}_2\text{N}]^-$. These results indicate that, as the pyridinium cation becomes less polar by increasing the length of the alkyl chain or by varying the position of a methyl group, the HBA of the anion increases, leading to a rise in β .

For our ionic liquids, as temperature rises, parameters α and β increase. This behavior is unexpected when compared to results in a previous study.¹⁶ Little information is available on the temperature dependence of Kamlet–Taft parameters for ionic liquids. The effect of temperature may be due to steric effects. We suggest that our measured hydrogen-bond donor and acceptor capabilities of pyridinium ionic liquids are influenced by steric effects that decline as temperature rises.

Conclusion

Polarity and Kamlet–Taft parameters were obtained for five pyridinium ionic liquids as a function of temperature. In this work, we investigated the influence of substituting a methyl group on the pyridinium cation on polarity and on Kamlet–Taft parameters in the range 25 to 65 °C. In addition, we studied the influence of the alkyl chain length on the cation on polarity and on Kamlet–Taft parameters in the range 25 to 65 °C. Polarities for the five pyridinium ionic liquids at 25 °C are close to those for short-chain alcohols and to those for imidazolium ionic liquids.

We find trends in the influence of substituting a methyl group and the influence of the length of alkyl chain on the pyridinium cation on polarity and on Kamlet–Taft parameters: Substituting a methyl group on the cation decreases polarity. Substituting a methyl group in the C(2) position on the cation leads to low

polarity and reduces the dependence of temperature on polarity. Similar behavior is shown for π^* , a measure of the ratio dipolarity/polarizability.

Substituting a methyl group in the C(2) position on the cation influences α and β ; substituting a methyl group in the C(2) position on the cation leads to reduced polarity, reduced ratio of dipolarity/polarizability, reduced hydrogen-bond-donating acidity, and to an increase in hydrogen-bond-accepting basicity.

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