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# Solvolysis of 2-adamantyl *p*-toluenesulfonate in ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate

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#### ABSTRACT

was found to be similar to that of ethanol.

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## Introduction

Ionic liquids have attracted much attention as a new type of solvents with properties interesting to many scientists and engineers in recent years.<sup>1-3</sup> Ionic liquids are fluid salts composed of stable organic cations and either organic or inorganic anions. Commonly used types of the ionic liquids include 1,3-dialkylimidazolium, alkylammonium, tetraalkylammonium, tetraalkylphosphonium, and N-alkylpyridinium salts formed with bis(trifluoromethylsulfonyl)imide, tetrafluoroborate, hexafluorophosphate, and perfluoroalkylsulfonate ions. They are also considered 'green solvents' in electrochemistry and organic synthesis due to their non-volatility, non-flammability, reusability, and high polarity. 1,3-Dialkylimidazolium-based ionic liquids such as [BMIM][BF<sub>4</sub>], [BMIM][Tf<sub>2</sub>N], [BMIM][PF<sub>6</sub>], and [BMIM][TfO] are popular among the known ionic liquids (Fig. 1).<sup>1–3</sup> The liquids have been used for solvolysis, nucleophilic reactions, electrophilic reactions, Diels-Alder reactions, and catalytic reactions.

Polarity, which is one of the most fundamental and important parameters for characterizing the solvent effect in chemical reactions, has been quantified by solvent polarity scales based on physicochemical properties such as rate constants, equilibrium constants, and spectral absorption shifts.<sup>1,2</sup> These scales include the solvent ionizing power, *Y*, derived from the rate constants of

 $S_N1$  solvolysis,<sup>4</sup> which is accelerated by polar solvents. Grunwald and Winstein defined Y using Eq. 1,

$$\log\left(k/k_0\right) = Y$$

The solvolytic rate constants of 2-adamantyl p-toluenesulfonate were determined in  $[BMIM][BF_4]$  in the

presence/absence of 2,6-lutidine by NMR measurements. The activation parameters suggest that the

reaction proceeded by  $k_c$  mechanism. The solvolysis quantitatively gave 2-adamantanol as a product

by the reaction with the water present in the ionic liquid. The solvent ionizing power of  $[BMIM][BF_4]$ 

where  $k_0$  is the first-order rate constant of the solvolysis of *tert*butyl chloride in 80% ethanol at 25 °C, and k is the corresponding rate constant in another solvent. Later, Bentley and Schleyer defined the solvent ionizing power for tosylates,  $Y_{\text{OTs}}$ , using the rate constants for 2-adamantyl *p*-toluenesulfonate (**1**, Fig. 1) as a reference substrate.<sup>5</sup> Although it is a secondary substrate, **1** solvolyzes by an  $S_N1$  (limiting) or  $k_c$  mechanism without nucleophilic solvent assistance at the rate determining step.

Creary reported the solvolytic rates for 1-adamantyl methanesulfonate and 2-adamantyl trifluoromethanesulfonate in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM] [Tf<sub>2</sub>N] (Fig. 1). The rates in the ionic liquid were not extraordinarily higher than those found in common polar protic solvents. The ionizing power of [BMIM][Tf<sub>2</sub>N] for the mesylate was comparable to that of ethanol.<sup>6</sup> Okamura and Usui investigated the solvolysis of 2-methyl-2-(*p*-methoxyphenyl)-1-propyl p-fluorobenzenesulfonate, which reacted via an aryl-assisted route (a  $k_{\Delta}$  process), in imidazolium-based ionic liquid [BMIM][PF<sub>6</sub>] and [EMIM][BF<sub>4</sub>].<sup>7</sup> Chiappe reported the reaction of 1-iodoadamantane with NaN<sub>3</sub> in [BMIM][PF<sub>6</sub>] and [BMIM][Tf<sub>2</sub>N].<sup>8</sup> 2-Bromoadamantane did not react with NaN<sub>3</sub> in ionic liquids due to low nucleofugality of the leaving group. Some other solvolytic studies have reported the effect of added ionic liquids in methanol and in benzyl alcohol.<sup>9</sup>





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**Figure 1.** Structures of 2-adamantyl compounds (**1** and **2**), [BMIM][Tf<sub>2</sub>N], [BMIM] [BF<sub>4</sub>], and [EMIM][BF<sub>4</sub>].

The value of the solvent ionizing power generally depends on the reference substrates and leaving groups. Herein we report a solvolytic study of **1**, which has been used as the most fundamental reference compound for the determination of the solvent ionizing power, in ionic liquid [BMIM][BF<sub>4</sub>] to investigate the effect of its solvent polarity on the rates of the  $k_c$  route. This is a novel kinetic estimation of the solvation effect of an ionic liquid. [BMIM][BF<sub>4</sub>] is one of the most commonly used ionic liquids in organic synthesis.<sup>2,3</sup>

## **Results and discussion**

lonic liquid [BMIM][BF<sub>4</sub>] was prepared by a method similar to those described in the literature.<sup>6,10,11</sup> [BMIM][Cl] was synthesized by the reaction of 1-methylimidazole with 1-chlorobutane in acetonitrile and was purified by recrystallization in acetonitrile-ethyl acetate. [BMIM][BF<sub>4</sub>] was prepared by exchanging the anion of [BMIM][Cl] with NaBF<sub>4</sub> twice. The purity of the ionic liquid was checked by NMR.

Kinetic studies were carried out by following the solvolysis with <sup>1</sup>H NMR spectroscopy. Aliquots of a solution of **1** in [BMIM][BF<sub>4</sub>] were sealed in ampules and were heated at 75, 100, and 125 °C for various reaction times. The products were extracted with ether and were analyzed by <sup>1</sup>H NMR. Tosylate **1** was found to give cleanly only 2-adamantanol (2) as the product by the reaction with the water present in the ionic liquid. Rate constants were determined from plots of  $\ln(1 - A_p/A_t)$  versus time, where  $A_p$  and  $A_t$ are the area of the H-2 signal for 2 and the total area of the H-2 signals for both 1 and 2, respectively. The formation of 2 was found to follow the first order kinetics, and the rate constants and activation parameters are summarized in Table 1. The activation entropy  $(\Delta S^{\ddagger})$  was small and slightly positive, suggesting that the reaction proceeds by the  $S_N 1$  mechanism, and that  $\mathbf{2}$  is unlikely to have formed by the nucleophilic attack on the sulfur atom of the p-toluenesulfonate group with S-O bond cleavage. The hydrolysis of sulfonate esters that proceeds via S-O bond fission is characterized by negative activation entropy, while nearly zero entropy is usually observed for a unimolecular reaction.<sup>12</sup>

The first-order rate constant of **1** at 25 °C was estimated to be  $8.0 \times 10^{-10} \text{ s}^{-1}$  by extrapolation of the data at other temperatures. The solvent ionizing power of  $Y_{\text{OTs}}$  for [BMIM][BF<sub>4</sub>] is calculated to be around -1.5, which is only slightly larger than that of ethanol ( $Y_{\text{OTs}} = -1.75$ ). These results are in line with the data for [BMIM] [Tf<sub>2</sub>N] reported by Creary.

Similarities to ethanol have been also reported in the research using the Dimroth–Reichardt  $E_{T}(30)$  scale.<sup>1b,13</sup> This scale is one of the most popular empirical polarity scales employing changes in the  $\pi$ - $\pi$ <sup>\*</sup> absorption band of solvatochromic 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridino)phenolate (Reichardt's betaine dye 30). The absorption is shifted to shorter wavelength with increasing solvent polarity. Systematic studies have demonstrated that 1.3-dialkylimidazolium salts are less polar than water, and are similar to polar organic solvents (methanol, ethanol, 1-propanol, and acetonitrile).<sup>1,13</sup> The  $E_{T}(30)$  scales of [BMIM][Tf<sub>2</sub>N], ethanol, [BMIM][BF<sub>4</sub>], 80% ethanol, and methanol have been determined to be 51.5, 51.9, 52.5, 53.7, and 55.8 kcal mol<sup>-1</sup>, respectively. [BMIM][BF<sub>4</sub>] is only slightly more polar than [BMIM][Tf<sub>2</sub>N] and ethanol.

The *Y* values are determined from kinetic data, which are correlated with microscopic change in solvation during the ionization.<sup>14</sup> Although it has been uncertain that the solvatochromic scale can apply to the heterolytic reactions in the ionic liquids, similar aspect was confirmed between  $Y_{\text{OTs}}$  and  $E_{\text{T}}(30)$  for [BMIM][BF<sub>4</sub>] and ethanol. Therefore, the effect of solvation by the ionic liquids on the heterolytic reactions could be interpreted using the  $E_{\text{T}}(30)$  scale.

The rate constant of **1** only slightly decreased in the presence of a 2,6-lutidine buffer. An addition of 3% water resulted in a 4-fold rate enhancement. The addition of 2,6-lutidine and the increase in water concentration did not influence effectively the solvolytic rates of this system.

Creary has found the large enhancement of the solvolysis rate for 1-adamantyl mesylate in [BMIM][Tf<sub>2</sub>N] by addition of small amounts of water, whereas the enhancement effect is small for the solvolysis of 1-(*tert*-butyl)-3,3-dimethyl-2-oxobutyl triflate that reacts via a  $k_{\Delta}$  route.<sup>6</sup> Since both 1 and 1-adamantyl mesylate are widely accepted to solvolyze through  $k_c$  process, the significant enhancement effect might be attributed to the mesylate leaving group. The ion pair return might be suppressed by increasing the rate for product formation process by the solvent attack at the ion-pair stage for the mesylate.

## Conclusion

In summary, the solvent ionizing power of [BMIM][BF<sub>4</sub>] based on kinetic measurements was found to be similar to that of

 Table 1

 Kinetic data for the solvolysis of 2-adamantyl p-toluenesulfonate (1) in [BMIM][BF4] (0.2 wt % H2O)

Run no.	2,6-Lutidine (M)	Temp (°C)	$k (s^{-1})$	$\Delta H^{\ddagger}$ (kcal mol <sup>-1</sup> )	$\Delta S^{\ddagger}$ (cal K <sup>-1</sup> mol <sup>-1</sup> )
1	None	125	$3.1  imes 10^{-4}$		
2	None	125	$4.0  imes 10^{-4}$		
3	None	125	$4  imes 10^{-4}$		
4	0.068	125	$2  imes 10^{-4}$		
5 <sup>a</sup>	0.068	125	$8.2  imes 10^{-4}$		
6	None	100	$3.2  imes 10^{-5}$		
7	None	100	$2.8  imes 10^{-5}$		
8	None	75	$1.3 imes 10^{-6}$		
		25	$8.0\times 10^{-10b}$	30	0.8

<sup>a</sup> 3% (v/v) of water was added.

<sup>b</sup> Extrapolated from data at the higher temperatures.

ethanol. The solvolysis of 1 in [BMIM][BF<sub>4</sub>] was found to give quantitatively **2** through the  $S_N1$  mechanism by the NMR analysis.

The present and further study of *Y* scale of ionic liquids would elucidate the microscopic effect of solvation of the ionic liquids during the heterolytic reactions that are used in synthesis of various functional compounds. Since the polarity of the ionic liquids can be tuned by changing the counter anion, comparison of the Y scale of the imidazolium-based ionic liquids with various anions will reveal the role of the anions, and the research will provide the fundamental data to develop fine-tuned ionic liquids as environmentally friendly (green) solvents with desired solvation effect for enhancement of product yield and selectivity.

## Experimental

NMR spectra were recorded on a 300 MHz spectrometer at room temperature. 2-Adamantyl p-toluenesulfonate (1) was prepared by the reaction of 2-adamantanol (2) with *p*-toluenesulfonyl chloride in the usual manner.<sup>15</sup> Ionic liquids [BMIM][Cl]<sup>10</sup> and [BMIM][BF<sub>4</sub>]<sup>11</sup> were prepared by methods similar to those reported in literature. The other reagents were commercially available and were used as received.

## Kinetics

The solvolvtic rates were determined using the usual sealed ampule technique. A solution of **1** (0.020 M) in [BMIM][BF<sub>4</sub>] was prepared, and glass ampules were filled with 0.5 mL aliquots of the solution and then sealed. These ampules were left in oil thermostats for desired periods of time. The contents of the ampules were extracted five times with ether. The combined ether lavers were concentrated and analyzed by <sup>1</sup>H NMR. Only **2** was detected as a product. The first-order rate constants were calculated using standard least-squares procedures.

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