J Solution Chem (2015) 44:1518–1528
DOI 10.1007/s10953-015-0356-7

Ionic Liquids: Additives for Manipulating the Nucleophilicity

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Received: 4 June 2014 / Accepted: 20 February 2015 / Published online: 17 July 2015

Abstract Kinetic investigations of the S_N2 reaction at the sulfur atom of *p*-toluenesulfonyl chloride with sodium azide in dried methanol in the presence of varying amounts of room temperature ionic liquids (RTILs), 1-butyl-3-methylimidazolium acetate ($[C_4C_1im][CH_3COO]$), 1-butyl-3-methylimidazolium chloride ($[C_4C_1im]Cl$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4C_1im][PF_6]$), were carried out in order to explore and understand the impact of these additives on the rate of such reactions. The observed results indicate that the rate constant of the reaction increase appreciably with increases in the concentration of RTILs in RTIL–methanol binary solvent systems. The results were analyzed in light of a Kamlet–Taft model system, which established that the observed impact of RTILs can be attributed to the cumulative effects of increase in the β value (hydrogen bonding acceptor ability) which is expected to enhance the reactivity of *p*-toluenesulfonyl chloride as well as the nucleophilicity of the azide ion and decrease in the π* value (solvent dipolarity/polarizability) which is expected to enhance the reactivity of the azide ion. Of the three ionic liquids used in the presented studies, $[C_4C_1im][CH_3COO]$ was observed to be more effective in accelerating the rate constant; this we attribute to its comparatively stronger ability to increase the β value and decrease the π* value in the mixed solvent system.

Keywords Ionic liquid (IL) · Nucleophilicity · Kinetics · RTILs · S_N2 reaction · Solvatochromism

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1 Introduction

Ionic liquids (ILs), because of their unusual and interesting physico-chemical properties [1–10], have emerged as front runners among eco-friendly solvents. During the last few decades researchers have been paying enormous attention towards exploration of the potentialities of ILs as solvents/catalysts/cosolvents for a variety of reactions of synthetic and industrial importance [10, 11]. The resulting studies have established ILs as very interesting reaction media which offer process advantages over molecular solvents. In many cases it has been reported that the IL specific effects cause the reactants to behave in a different way than they do in molecular solvents [12, 13]. Recent investigations related to the use of ILs as solvents in chemical transformations, besides leading to discovery of their useful multidimensional features, have also highlighted some serious procedural concerns associated with the use of ILs as reaction media. In this regard the foremost concerns are the high viscosity, slow reorganization and high solvent reorganization energies of ILs that often slow down the kinetics of chemical transformations [12, 14–17]. In view of the above cited potentialities and concerns related to IL mediated chemical transformations, researchers have started exploring the use of ILs as additives/cosolvents with conventional solvents. Interestingly, the IL + cosolvent mixtures in some cases have been reported to possess altered and improved physicochemical properties [18–22]. Such properties in certain cases have proved to be very advantageous for the understanding of mechanistic and kinetic aspects of the attempted chemical transformations.

In view of the above cited reasons, we initiated a series of studies aimed at exploring the impact of ILs on physicochemical properties of conventional reaction solvents [23–25]. Kinetic investigations on classic solvent sensitive reactions such as nucleophilic substitution reactions [26–29] provide a useful and reliable means for exploration and understanding of the variations in solvent properties on account of additives. For the present work we carried out detailed kinetic investigations on the nucleophilic substitution reaction of *p*-toluenesulfonyl chloride with sodium azide (NaN_3) in binary solvent systems comprised of IL and methanol. The Kamlet–Taft model was used to analyze the IL influence on the kinetic aspects of the investigated reaction. The results presented establish that the imidazolium-based ILs enhance the reactivity of both substrate (electrophilicity), as well as nucleophile (nucleophilicity of ionic nucleophiles, such as azide ion), in S_N reactions involving neutral substrate and charged nucleophile.

2 Experimental Section

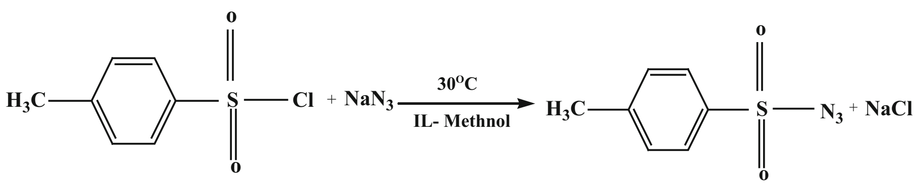
2.1 Materials

Sodium azide and *p*-toluenesulfonyl chloride were obtained from E-Merck. *p*-Nitroanisole and *p*-nitroaniline were obtained from Sigma–Aldrich. 1-Methylimidazole and 1-chlorobutane used for the synthesis of ILs were obtained from Spectrochem (India). Acetonitrile (GR grade, 99.9 %), methanol (GR grade, 99.9 %), ethyl acetate (GR grade, 99.5 %) and dichloromethane (GR grade, 99.5 %) procured from Merck–India were purified and dried as per the standard methods [30]. Spectroscopic grade ILs, viz. $[C_4C_1im]Cl$, $[C_4C_1im][CH_3COO]$ and $[C_4C_1im][PF_6]$, were synthesized as per literature procedures [23, 31–33]. In the first step of the synthesis, 1-methylimidazole was refluxed with *n*-butyl chloride for 90 h under argon to get 1-butyl-3-methylimidazolium chloride as a white crystalline solid. In the next step, the halide ion Cl^- was exchanged with PF_6^- or CH_3COO^- on treatment with HPF_6 or CH_3COONa to get $[C_4C_1im][PF_6]$ or $[C_4C_1im][CH_3COO]$ respectively. The ILs were dried and stored in a desiccator under inert atmosphere and were characterized through ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The water content of these ILs was analyzed by Karl Fischer titration and were restricted to <50 ppm.

2.2 Kinetic Procedure

The reaction between *p*-toluenesulfonyl chloride and sodium azide was carried out under pseudo-first order conditions using an excess of sodium azide (NaN_3) by a factor of (1:10). In the kinetic runs the reaction mixture in a 1 cm quartz cuvette was monitored for the decrease of absorbance corresponding to *p*-toluenesulfonyl chloride at appropriate wavelength (243–245 nm) until at least a degree of advancement of 80 % for the reaction. The kinetic investigations were carried out by using a Shimadzu 1650 PC UV–Visible Spectrophotometer equipped with thermostat for controlling the temperature with an accuracy of 0.1 °C. All the experiments were carried out at a fixed temperature of 30 °C.

In a typical kinetic experiment, 2 mL of stock solution was prepared by dissolving 0.0381 g of *p*-toluenesulfonyl chloride (0.1 $mol \cdot L^{-1}$) in pure and dried methanol. A 0.33 $mmol \cdot L^{-1}$ solution of *p*-toluenesulfonyl chloride in the dried methanol was prepared by taking 10 μL of stock solution using a micro pipette. Dried methanol was used in order to avoid the complications of solvolysis of *p*-toluenesulfonyl chloride in moist methanol or methanol having small amounts of pyridine [34, 35], which is better evidenced by the appearance of similar spectra of the substrate, i.e. *p*-toluenesulfonyl chloride taken at different time interval within the time domain of the kinetic investigation. Also, 0.15 $mol \cdot L^{-1}$ solution of NaN_3 (0.0195 g) in methanol was prepared and 50 μL of this stock solution were added to methanol in a cuvette to prepare a 2.5 $mmol \cdot L^{-1}$ solution of sodium azide. Thus in the 3 mL solution taken in the cuvette, the concentration of *p*-toluenesulfonyl chloride (0.33 $mmol \cdot L^{-1}$) and sodium azide (2.5 $mmol \cdot L^{-1}$) were fixed in a typical experimental run. Similar experimental runs were carried out in the presence of varying concentrations of the RTILs $[C_4C_1im]Cl$, $[C_4C_1im][CH_3COO]$ and $[C_4C_1im][PF_6]$ in methanol. For solvatochromic studies, the absorption patterns of the dyes *p*-nitroanisole and *p*-nitroaniline in IL–methanol binary mixtures of varying compositions were recorded. The characteristic absorption patterns of these dyes were analyzed for the estimation of IL concentration dependent Kamlet–Taft parameter values, viz. π^* and β of the used IL–methanol binary mixtures [36].



(1) (2) (3) (4)

Scheme 1 Nucleophilic substitution reaction between *p*-toluenesulfonyl chloride (*1*) and sodium azide (*2*) to form *p*-toluenesulfonyl azide (*3*) and sodium chloride (*4*)

3 Results and Discussion

Investigations on the reaction between *p*-toluenesulfonyl chloride (1) and sodium azide (2), as presented in Scheme 1, were carried out in dried methanol and IL–methanol binary solvent systems in order to explore and understand the impact of imidazolium based ILs as additives on the kinetics of nucleophilic substitution reactions. The reaction is reported to follow first order kinetics with respect to each reactant [37]. In the present kinetic studies, all the experiments were performed at 30 °C and in presence of excess of the nucleophile azide anion. Under such experimental conditions, where the kinetic role of sodium azide was nullified by taking the same in excess, the reaction is expected to follow pseudo-first order kinetics [37]. Figure 1 shows a typical kinetic plot recorded for the reaction between *p*-toluenesulfonyl chloride with excess concentration of sodium azide. The data fit well to the integral rate law corresponding to a pseudo-first order reaction with $R^2 = 0.99$. In view of this observation, the kinetic data recorded for the reaction in three types of IL–methanol solvent mixtures, viz. $[C_4C_1im][CH_3COO]$–methanol, $[C_4C_1im]Cl$–methanol and $[C_4C_1im][PF_6]$–methanol, with varying IL concentrations, were analyzed using Eq. 1:

$$k_{obs} = \frac{1}{t}\ln\left(\frac{A_0}{A_t}\right) \quad (1)$$

where, k_{obs} is the pseudo-first order rate constant, A_0 is the absorbance at the time of initiation and A_t is the absorbance at time t after the initiation. The estimated values of k_{obs} for the investigated nucleophilic substitution reaction are tabulated as Table 1. The values of the rate constants in Table 1 are an average of results from three kinetic runs recorded under similar conditions. The results from different runs were observed to be reproducible within ±5 %. As is clear from these values, the addition of imidazolium based ILs to methanol increases the rate constant for the nucleophilic substitution reaction, depending upon the nature and concentration of the added IL. In the recent past many groups have investigated the impact of ILs as solvents on the kinetics of diverse type of nucleophilic substitution reactions [13, 38–45]. In these studies, in many cases ILs have been found to affect the kinetics in the same way as molecular solvents, while in many other cases they have also been found to exhibit IL specific effects on the kinetics of the investigated

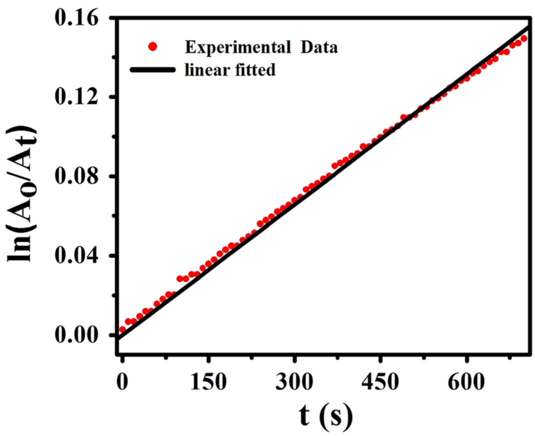


Fig. 1 Kinetic plot recorded for the reaction between sodium azide (NaN_3) and *p*-toluenesulfonyl chloride in methanol as solvent at 30 °C. The *solid line* shows the fit of the data to the integral rate law corresponding to the pseudo-first order kinetic equation ($R^2 = 0.99$)

Table 1 Pseudo-first order rate constant (k_{obs}) for the reaction between sodium azide (NaN_3) and *p*-toluenesulfonyl chloride in IL–methanol solvent media at 30 °C

Concentration (mol·L^{-1})	Rate constant (k_{obs}) × 10^4·s^{-1} at 30 °C
$[C_4C_1im][CH_3COO]$	
0.000	2.19
0.052	2.34
0.156	4.62
0.261	8.24
0.362	12.00
0.468	24.10
0.520	36.80
$[C_4C_1im]Cl$	
0.000	2.19
0.059	3.85
0.170	6.37
0.291	6.91
0.410	8.29
0.532	9.83
0.590	10.10
$[C_4C_1im][PF_6]$	
0.000	2.19
0.047	4.60
0.142	4.99
0.240	5.64
0.330	6.02
0.420	7.02
0.470	7.46

reactions. The kinetic effects have been explained in light of microscopic solvent polarity parameters and/or specific IL-reactant/activated complex/product interactions. The results of the present study seem to suggest a specific impact of ILs on the solvent–activated complex interactions that in turn are responsible for the variations observed in the kinetics.

Mechanistically the nucleophilic substitution reaction between *p*-toluenesulfonyl chloride and sodium azide is a S_N2 reaction of type 1, i.e. a charged nucleophile (N_3^-) reacting with neutral substrate (*p*-toluenesulfonyl chloride) [37, 46]. S_N reactions at sulfur are facilitated by the presence of vacant d-orbitals, which interact with the nucleophile to give rise to a reasonably stable transition state. In the present case, it is implied that the activated complex $Y^{\delta-}\cdots R\cdots X^{\delta-}$ formed during the course of reaction shall have a charge similar to that of reactants. However, in comparison to the reactants, the charge density on the activated complex would be lower. Since the activated complex is associated with a decrease in overall charge separation, the reaction is expected to be promoted by relatively less polar media. According to the Hughes–Ingold rules [47], the rate of such reactions should decrease with increasing polarity of the solvent. Assuming imidazolium based ILs to behave as salts, this implies that with the increase in concentration (mol·L^{-1}) of ILs in methanol, the effective ion concentration in the solvent media will increase and hence the rate constant is expected to decrease, which is quite opposite to our observations. The present investigation then is one of the examples where the observed results can't be explained in light of the Hughes–Ingold model, according to which the solvent–solute interactions are solely electrostatic in nature. In the past such observations have been explained and analyzed by using the linear solvation energy relationship (LSER) model set by Kamlet and Taft [48–52], which takes into account all specific interactions that can contribute to solvent effects on the overall kinetics of reactions. According to these studies the solvent systems can not only change the absolute reaction rate through enhancing the reactivity of the substrate [42] but also the relative nucleophilicities of nucleophiles [40, 53]. The resultant impact on the reaction kinetics can be quantified through the equation developed by Kamlet and Taft [48–52] as presented in Eq. 2:

$$\ln(k) = \ln(k_0) + a\alpha + b\beta + s\pi* \tag{2}$$

where $\ln(k_0)$ is the intercept and a, b and s are the indicators of sensitivity of the process to the solvent characteristics α, β and π^*. The parameter α is a quantitative scale of hydrogen bond acidity of a solvent or its ability to donate a hydrogen bond, β is a scale of hydrogen bond basicity of the solvent or its ability to accept a hydrogen bond and π^* is the solvent dipolarity/polarizability, which is a scale of the ability of the solvent to stabilize a charge or dipole. The values of these parameters as reported in literature for methanol and the pure imidazolium based ILs [54–58] used in the present study are presented in Table 2.

Solvatochromic studies on binary solvent mixtures of ILs [59] in molecular solvents have established that addition of the former to the latter changes the microscopic parameters α, β and π^*, in a concentration dependent manner, with values moving towards those of the pure ILs. Since the Kamlet–Taft parameter α, which gives the hydrogen bond acidity of the solvent, is largely characteristic of the cation of the IL and is insignificantly affected by the anion [60], the α values of the investigated systems were expected to be the same for all ILs used in the present investigation. In view of these above cited reports we carried out the solvatochromic study of the IL–methanol solvent systems used for the present kinetic investigations. The dyes *p*-nitroanisole and *p*-nitroaniline were employed for the estimation of Kamlet–Taft parameter values π^* and β by Eqs. 3 and 4, respectively [36]:

$$\pi^* = 14.57 - \frac{4270}{\lambda_{\max}} \tag{3}$$

$$\beta = 11.134 - \frac{3580}{\lambda_{\max}} - 1.125 \times \pi^* \tag{4}$$

In the solvatochromic studies it was observed that while the value of π^* decreases, the β parameter increases with increase in IL concentration, the extent of change being sensitive to the nature of the IL. The recorded variations in π^* and β as a function of IL concentration are presented in Figs. 2 and 3, respectively. As is evident from these plots the values of π^* vary with concentration of the IL with an extent that varies with the nature of anions in the sequence $[C_4C_1im][CH_3COO] < [C_4C_1im]Cl = [C_4C_1im][PF_6]$. The

Table 2 Kamlet–Taft parameters for the pure solvents used in this work

Solvent	α	β	π^*
Methanol [45, 54]	0.76	0.61	0.73
$[C_4C_1im][PF_6]$ [55–58]	0.68	0.21	1.02
$[C_4C_1im]Cl$ [55–58]	0.48	0.94	1.02
$[C_4C_1im][CH_3COO]$ [56–58]	0.57	1.18	0.89

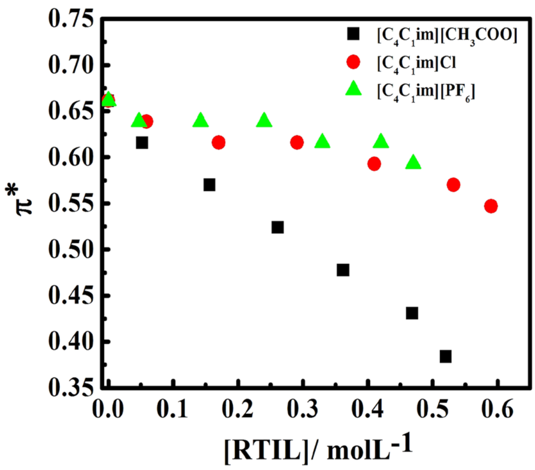


Fig. 2 Plot showing variation of π^* with changing concentration of IL in methanol–IL solvent systems. The *values* depicted are based on spectrophotometric responses of the dye *p*-nitroanisole in the used solvent systems (Eq. 3)

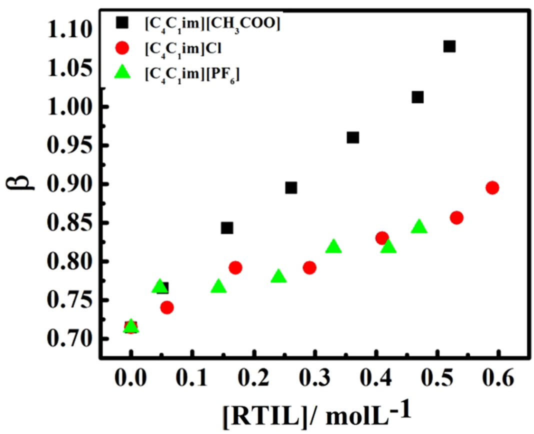


Fig. 3 Plot showing variation of β with changing concentration of IL in methanol–IL solvent systems. The *values* depicted are based on spectrophotometric responses of the dye *p*-nitroaniline in the used solvent systems (Eq. 4)

comparatively large decrease in π^* on addition of IL to methanol in the case of [C_4C_1-im][CH_3COO] is probably because of the weak coulombic interaction among constituents of this IL due to greater charge delocalization on CH_3COO^-. The decrease of π^* values with increase in concentration of IL is expected to stabilize the azide ion and hence the extent of the same will be lowest in case of [C_4C_1im][CH_3COO]. In contrast to π^*, the β parameter was observed to increase with increases in the concentration of the ILs. The extent of increase in the β value was observed to follow the trend [C_4C_1im][CH_3-COO] > [C_4C_1im]Cl = [C_4C_1im][PF_6], which matches the conjugate basicities of the IL anions. Thus the increase in β with increasing concentration of ILs is an indicator of increase in basicity of the solvent mixture. The enhanced basicity of the solvent mixture is expected to enhance the chances of hydrogen bond formation between the methyl protons of *p*-toluenesulfonyl chloride with the IL counter anions. These interactions in turn will lead to decreases in the electron charge density around the sulfonyl sulfur and hence enhance the reactivity of the substrate, i.e. *p*-toluenesulfonyl chloride [42]. Moreover, an increase in β is expected to increase the basicity of the medium that in turn will increase the nucleophilicity of the negatively charged azide anion. In view of expected insensitivity of α towards the nature and concentration of the IL used, Eq. 2 for the presented results can be written as Eq. 5:

$$\ln(k) = \ln(k_{\mathrm{MeOH}}) + b\beta + s\pi^{*} \quad (5)$$

where k_{MeOH} is the apparent rate constant of the investigated reaction in absence of IL. Multivariant regression was used to fit the rate constant (k_{obs}) to the experimentally determined solvent polarity parameters β and π^* through Eq. 5 using b and s as adjustable parameters. This process yielded the Eqs. 6, 7 and 8 for the three IL–methanol solvent systems, i.e. $[C_4C_1im][CH_3COO]$–methanol, $[C_4C_1im]Cl$–methanol and $[C_4C_1im][PF_6]$–methanol, respectively.

$$\ln(k) = -8.43 + 4.67\beta - 5.62\pi^{*} \quad (6)$$

$$\ln(k) = -8.43 + 3.98\beta - 3.46\pi^{*} \quad (7)$$

$$\ln(k) = -8.43 + 3.64\beta - 3.08\pi^{*} \quad (8)$$

These equations clearly establish that the rate enhancement on account of IL addition is due to cumulative impact of the variation in both β and π^*. The higher degree of confidence in the value of s (−5.62) in the case of the $[C_4C_1im][CH_3COO]$–methanol solvent systems indicates that the π^* value of this solvent mixture is the dominant factor in enhancing the rate constant of the reaction. Therefore, the polarizability of the solvent mixture, i.e. π^*, seems to dominate the rate enhancement to which the variation of β also contributes positively. In the case of $[C_4C_1im]Cl$–methanol and $[C_4C_1im][PF_6]$–methanol systems the higher sensitivity values in b (3.98 and 3.64 respectively) indicates that β in these solvent systems is the dominant factor in accelerating the rate of reaction. Thus solvent systems with higher values of β exhibit higher rates. The strength of this theory is portrayed in Fig. 4 which shows excellent correlation between predicted and experimental values of ln k in the case of the $[C_4C_1im][CH_3COO]$–methanol solvent system and also holds good for other solvent media. In light of the above cited inferences, observations and recorded variations in β and π^* with increase in concentration of IL, the k values for the investigated nucleophilic substitution reaction are expected to increase in the order $[C_4C_1im][CH_3COO] \gg [C_4C_1im]Cl > [C_4C_1im][PF_6]$, a trend that matches our observations.

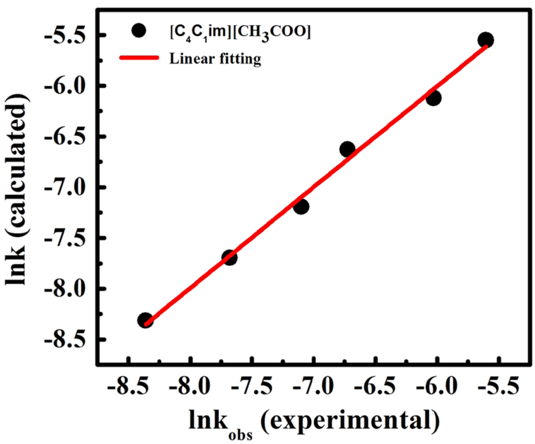


Fig. 4 Plot of ln k calculated from the Kamlet Taft LSER fit versus ln k_{obs} for the nucleophilic substitution reaction in $[C_4C_1im][CH_3COO]$–methanol solvent systems. *Solid line* shows the linear fit with $R^2 = 0.99$

Thus the highest rate achieved in the $[C_4C_1im][CH_3COO]$–methanol solvent systems is because of the cumulative effects of the large β values, which reflects their highly basic character, and the more dominating small π^* values which synergistically enhance the rate of the reaction by enhancing the reactivity of the substrate and nucleophilicity of the negatively charged azide ion.

4 Conclusions

The impact of imidazolium based ILs on the reaction kinetics of nucleophilic substitution reaction between *p*-toluenesulfonyl chloride and sodium azide in methanol was investigated. It was observed that addition of RTILs increases the rate kinetics in the order $[C_4C_1im][CH_3COO] \gg [C_4C_1im]Cl > [C_4C_1im][PF_6]$. Solvatochromic studies of the used solvent systems establish that the observed results can be explained in light of the multi parameter Kamlet–Taft equation. For the nucleophilic substitution reaction under study, it was inferred that the increase in β value and decrease in the π^* value of the solvent system, on addition of imidazolium based ILs, are the two factors that through a synergistic impact enhance the kinetics of, S_N reaction involving *p*-toluenesulfonyl chloride and sodium azide.

Acknowledgments MAB thanks Department of Science and Technology, New Delhi, India, for the research grant No. SR/S1/PC-11/2009. MAR thanks CSIR for the financial assistance.

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