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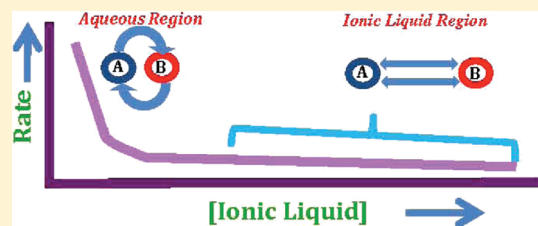
The Cosolvent-Directed Diels–Alder Reaction in Ionic Liquids

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Supporting Information

ABSTRACT: The rate constants of a bimolecular Diels–Alder reaction in binary mixtures of ionic liquids prepared in molecular solvents were analyzed to investigate the effect of viscosity of the medium and solvent effect. In this connection, we have carried out the Diels–Alder reaction of anthracene 9-carbinol with *N*-ethyl maleimide in binary mixtures of pyridinium-based ionic liquids, 1-butyl-pyridinium tetrafluoroborate, 1-butyl-3-pyridinium tetrafluoroborate, and 1-butyl-4-methyl pyridinium tetrafluoroborate in water, methanol, and chloroform at 298.15 K. The rates of reaction decreased, caused by gradually increasing the volume fraction of ionic liquids in solvents for all three ionic liquids. The kinetic results demonstrate a successful application of the pairwise interaction model built upon the concept of enforced hydrophobic hydration. A temperature-dependent study of kinetics of the Diels–Alder reaction was carried out in the binary mixtures of ionic liquids in water and was explained by the entropy–enthalpy compensation effect based upon activation parameters. Kinetics of the Diels–Alder reaction in highly aqueous medium was noted to be entropically driven.



INTRODUCTION

In recent years, room temperature ionic liquids have been used as catalyst to realize several organic reactions. Ionic liquids have recently been considered as an alternative to replace volatile organic solvents in chemical processes, because of their special interesting physicochemical properties.^{1–4} Ionic liquids possess insignificant vapor pressures, are nonflammable, and can dissolve different types of compounds. Their physical properties may be tuned by varying the structures of their ions. Out of several reactions, the Diels–Alder reaction is one of the important C–C bond forming reactions used for manufacturing six-membered rings with fine control over stereoselectivities of the products.⁵ The Diels–Alder reactions normally should exhibit small solvent effects in organic solvents due to the presence of isopolar activated complex.⁶ However, the rate enhancement of a Diels–Alder reaction in water opened doors for future research on solvent effect on the kinetics of a Diels–Alder reaction. The rate constants of the Diels–Alder reactions in water are much higher than those noted in organic solvents, establishing the important role of water in realizing organic reactions.⁷ In addition to obvious economical and environmental advantages, water is known to have surprising beneficial effects on the kinetics of organic reactions.^{7–12} Studies on solvent effects are generally carried out by means of relationships between reactivity properties that are reaction rate or several types of selectivity and empirical parameters representing different kinds of solute–solvent interactions.^{13–15} Gajewski proposed an effective correlation between rate constants of four different reactions and cohesive energy densities of solvents and solvation parameters.¹⁵ The studies carried out in the recent past have demonstrated that ionic liquids can influence the kinetics of these reactions.^{16–20} A previous report from this laboratory has demonstrated that rates of intermolecular Diels–Alder reaction of cyclopentadiene with methyl, ethyl, and butyl acrylates in

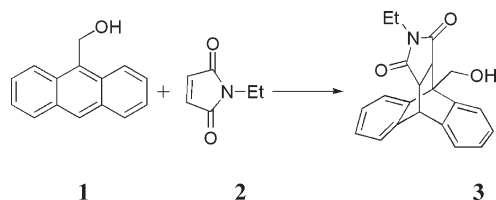
different ionic liquids are slowed down due to high viscosity of ionic liquids,²¹ since it will be difficult for reactants to interact with each other due to dense solvent environment. However, the role of viscosity in ionic liquids on an intramolecular Diels–Alder reaction of (*E*)-1-phenyl-4-[2-(3-methyl-2-butenyloxy)benzylidene]-5-pyrazolone was analyzed using theoretical models to recommend the predominant role of microviscosity rather than of the bulk macroscopic viscosity.²² An earlier report from our group has demonstrated that the addition of cosolvents to ionic liquids brings a dramatic decrease in the viscosity of the solution.²³ Since the solvent mixture consisting of an ionic liquid and a cosolvent is less viscous, it may act as effective solvent medium for carrying out organic reactions. The extent of decrease in viscosity of the ionic liquids depends on the nature and amount of the cosolvent added. Further, the polarity of the solvent mixture can also influence the kinetics of organic reactions. In this connection polarity parameters electronic transition energy E_T^N , hydrogen bond donor ability; acidity α , hydrogen bond acceptor ability; basicity β and polarizability π^* of pure ionic liquids and ionic liquid–cosolvent binary mixtures have been investigated.^{24,25} The nonideality in the polarity parameters in the ionic liquid–cosolvent mixtures indicated solute–solvent interactions that can influence the rates and selectivities of organic processes in a remarkable manner. In continuation of our ongoing work on ionic liquids,^{26,27} we now examine the issue of whether newly created solvent media comprising ionic liquids and cosolvent can influence the rates and stereoselective reactions of a popular bimolecular organic reaction, i.e., the Diels–Alder reaction. The

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Scheme 1



Diels–Alder reaction between anthracene-9-carbinol (**1**) and *N*-ethylmaleimide (**2**) (Scheme 1) has been studied in different binary mixtures of the pyridinium-based ionic liquids with molecular solvents. The relative effect of viscosity of the medium in relation to the other solute–solvent interactions in governing the organic reaction has been discussed. The activation parameters for the reaction **1** + **2** have been determined from temperature-dependent kinetics in the [BP][BF₄] + H₂O, which was selected as a model system, based on which the nature of the solute–solvent interactions has been discussed.

EXPERIMENTAL SECTION

Materials. Pyridine was obtained from M/s. Spectrochem and was distilled prior to its use. 3-Picolene, 4-picolene, and *N*-ethyl maleimide were purchased from M/s. Aldrich. Anthracene-9-carbinol and sodium tetrafluoroborate (NaBF₄) were used as obtained. All the organic solvents used for preparing binary mixtures with ionic liquids were spectroscopic grade. Deionized water with specific conductance of $0.55 \times 10^{-6} \text{ S cm}^{-2}$ was used for preparing mixtures of ionic liquids. Ionic liquids used in the present investigation were synthesized and purified according to the reported procedures.²⁸ The ionic liquids were synthesized in two steps. The first step included the synthesis of organic cation and the second the addition of anion.²⁸ The ionic liquids were characterized by ¹H NMR spectroscopy. The ionic liquids were dried under vacuum in order to remove excess water, and water content of the ionic liquids was measured before making solution by a Karl Fischer coulometer and did not exceed 30 ppm for any sample. The mixtures of ionic liquids with solvents were prepared on the basis of the volume fraction, V_f , defined as the ratio of volume of the ionic liquid to volume of the solution. Thus, the volume fraction of the ionic liquid $V_{f,2}$ is

$$V_{f,2} = 1 - V_{f,1} \quad (1)$$

where $V_{f,1}$ is volume fraction of solvents.

Kinetic Measurements. A 0.022 g quantity of anthracene-9-carbinol (**1**) was dissolved in 5 mL of methanol prior to use to give a 0.021 M stock solution. Fourteen microliters of the stock solution was added to 1 mL of the ionic liquid–solvent binary mixture resulting in 0.3 mM solution of **1** and equilibrated at the desired temperature for 10–15 min. A 0.070 g portion of *N*-ethyl maleimide (**2**) was dissolved in 5 mL of the methanol to yield a 0.112 M stock solution of the **2**. Twenty-five, 50, 75, and 100 μL of 0.112 M stock solution of **2** were then added to the cuvette containing 1 mL of the binary mixture of ionic liquids in solvents to give final concentration 2.8, 5.6, 8.4, 11.2 mM, respectively. The progress of the reaction was monitored by following the time-dependent decay of the absorbance peak of **1** at $\lambda = 380 \text{ nm}$. Since the concentration of **2** is higher than that of **1**, the time dependence of the decay is calculated to give pseudo-first-order rate constants, k' . Four values pseudo-first-order rate constants

were used to determine the second-order rate constants k_2 . The reported rate constants are an average of at least three kinetic runs on different samples and were reproducible to within $\pm 5\%$. The temperature of the cell was controlled using the single cell accessory having an accuracy of $\pm 0.1^\circ \text{C}$.

RESULTS AND DISCUSSION

The Diels–Alder reaction of **1** and **2** (Scheme 1) was carried out in the binary mixtures of pyridinium-based ionic liquids, namely, 1-butyl-pyridinium tetrafluoroborate, [BP][BF₄], 1-butyl-3-methyl-pyridinium tetrafluoroborate, [3-MBP][BF₄], and 1-butyl-4-methyl-pyridinium tetrafluoroborate, [4-MBP][BF₄], in molecular solvents like water, methanol, and chloroform. The nature of the cosolvent was an important determinant of the solute–solvent interactions, viscosity, and the resulting kinetic parameters.

The above reaction was fastest in water alone when compared to methanol, chloroform, and other ionic liquids. While the rate enhancement of the Diels–Alder reaction was first noted by Rideout and Breslow,^{8a} the comparatively lower the reaction rates in ionic liquids as compared to that in water by Tiwari and Kumar who demonstrated that higher viscosities of ionic liquids were detrimental to the progress of the reaction.²¹ A similar situation is seen in the present context. For example, the reaction selected by us in the present study was about 450–600 times higher than in any ionic liquids examined here. However, the reaction was about 10 times faster in organic solvents than in these ionic liquids.

The role of viscosity on the kinetics of Diels–Alder reactions was studied by Firestone and Vitale and others.²⁹ These authors noted that the slope of relative rates versus relative viscosities for an intramolecular Diels–Alder reaction was much greater than the one noted during the kinetic study of Claisen rearrangement in these solvents. Diels–Alder reactions share some common features with the Claisen rearrangement like low solvent dependence, unrelated to polarity. The dimerization of cyclopentadiene was also examined with respect to the viscosities of different solvents, and a linear increase in the dimerization rate was seen.^{30,31} From these examples, it is clear that in the lower end of viscosity scale the increase in the rates is sharp with viscosity. The reaction rates level off at $\sim 1.3 \text{ cP}$ before dropping with increasing viscosity above $\sim 1.3 \text{ cP}$. The 1,3 dipolar cycloaddition of diphenyldiazomethane with ethyl phenylpropionate was found to be enhanced with the rise in viscosity of different solvents to about $\sim 1 \text{ cP}$. Above 1 cP, a decline in the reaction rates was observed.³⁰ From the above examples it is clear that rates of different Diels–Alder reactions vary with the solvent viscosities. Both the rate increase and fall are seen in the viscosity range observed above. This observation is not yet understood on a molecular level. However, the rate enhancement in the low viscosity range cannot be accounted for in terms of current kinetic theory, as the bond-forming reactions are independent of viscosity in this collision-controlled regime. Firestone and co-workers have interpreted this behavior in terms of the vibrational activation theory.^{29,30,32} Accordingly, high vibrational and low translational energies (favored with increasing viscosity) promote the bond-making. The translational mode of a molecule is retarded with increasing viscosity resulting into the shifting of the translational to the vibrational mode. At very high viscosities, the situation pertains to an encounter-controlled regime. In this regime, the relative freedom of movement of the reactants in the

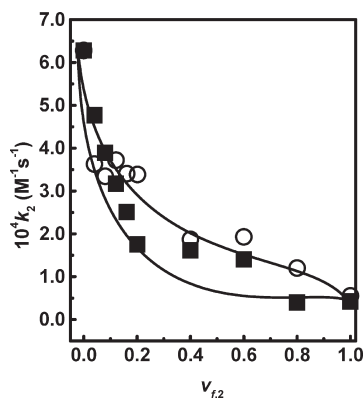


Figure 1. The plots of rate constants k_2 vs $V_{f,2}$ for binary mixtures of [4-MBP][BF₄] (■) and [3-MBP][BF₄] (○) in chloroform.

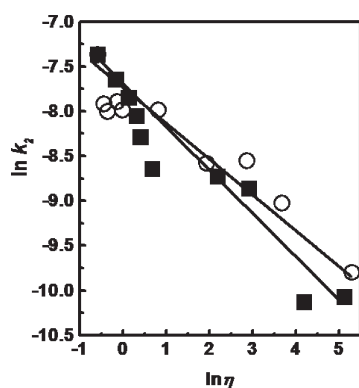


Figure 2. The plots of $\ln k_2 - \ln \eta$ in binary mixtures of [3-MBP][BF₄] (■) and [4-MBP][BF₄] (○) in chloroform at 298.15 K.

microenvironment of the encounter pair become limited. In such a highly viscous environment, reactants cannot see each other, consequently slowing down the reaction.

a. Ionic Liquid–Chloroform Binary Mixtures. Figure 1 shows second-order rate constants k_2 for the Diels–Alder reaction of **1** with **2** in the binary mixtures of pyridinium-based ionic liquids in chloroform as a function of the volume fraction of the second component in the binary mixture, i.e., ionic liquid, $V_{f,2}$.

The rate constant k_2 decreases with an increase in concentration of ionic liquids in the binary mixture. Kinetic measurements were limited to two pyridinium-based ionic liquids, [3-MBP][BF₄] and [4-MBP][BF₄], since [BP][BF₄] is insoluble in chloroform due to polarity difference and forms a biphasic system. In order to assess the role of viscosity, the rate constants were also plotted as a function of viscosity (Figure 2). The monotonic decrease confirms the fact that in the ionic liquid–chloroform system the rate of the reaction is primarily dominated by the viscosity of the reaction medium, rather than any other solute–solvent interactions.

In terms of solute–solvent interactions, the uniformity in the trend indicates an absence of any highly specific interactions between the reactants and the components of the binary mixture. The intermediate polarity of chloroform is apparently compatible with that of the ionic liquids used, which are known to have similar polarity ranges. It is noteworthy that the sensitivity of the rate constants is greater for the compositions within the lower viscosity range. This could be accounted for by the fact that the

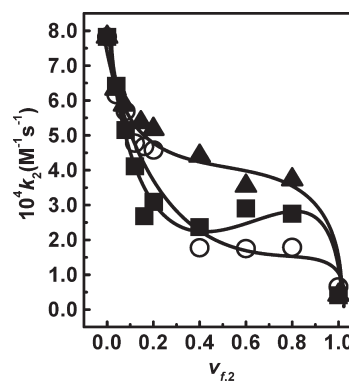


Figure 3. The plots of rate constants k_2 vs volume fraction of ionic liquid, $V_{f,2}$ for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (○), and [4-MBP][BF₄] (▲) in methanol 298.15 K.

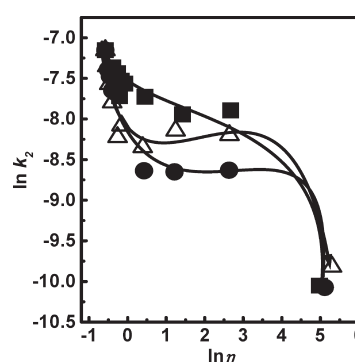


Figure 4. The plots of $\ln k_2 - \ln \eta$ for binary mixtures of [BP][BF₄] (■), [3-MBP][BF₄] (●), and [4-MBP][BF₄] (△) in methanol.

extent of reactivity damping by high friction can be saturated beyond a certain limit.

b. Ionic Liquid–Methanol Binary Mixtures. Rate constants k_2 for the Diels–Alder reaction **1** and **2** in binary mixtures of all three ionic liquids ([BP][BF₄], [3-MBP][BF₄], and [4-MBP][BF₄]) with methanol studied at 298.15 K show different behaviors as compared to ionic liquid–chloroform mixtures (Figure 3). The rate constants for the Diels–Alder reaction in the binary mixtures of ionic liquids in methanol decrease with the addition of ionic liquids to methanol in a sigmoidal form (Figure 4). The remarkable variation can be attributed to the fact that in addition to the viscosity of the medium, additional solute–solvent specific interactions seem to play a decisive role in determining the reactivity. The polarity of methanol differs significantly from that of the pyridinium ionic liquids. Methanol is also capable of forming hydrogen bonding with a wide variety of substrates.

The spatial inhomogeneity resulting from such binary mixtures was manifested as preferential solvation of the spectroscopic polarity probes.²⁵ In the present system, a similar preferential interaction between the reactant/the transition state with either of the components of the binary solvent mixtures is certainly plausible. The resulting solute–solvent specificity can overcome the effect of frictional forces in terms of decreasing viscosity. For the Diels–Alder reaction between **1** and **2**, it is seen that the rate constants remain at a nearly constant value—a “plateau”—in the intermediate composition range, where the increasing concentration of ionic liquids causes a 10-fold increase in viscosity.

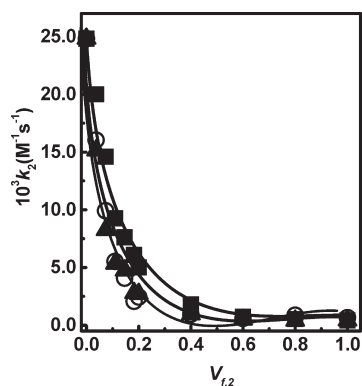


Figure 5. The plots of rate constants k_2 vs $V_{t,2}$ in the binary mixtures of $[\text{BP}][\text{BF}_4]$ (■), $[\text{3-MBP}][\text{BF}_4]$ (○), and $[\text{4-MBP}][\text{BF}_4]$ (▲) in water at 298.15 K.

The reactant/transition state does not experience the rising ionic liquid proportion coupled with a concomitant decrease in methanol concentration. The observations are indicative of the preferential solvation of the reactant/transition state by the methanol molecules or hydrogen bond donor (HBD)–hydrogen bond acceptor (HBA) complex formed between ionic liquids and methanol rather than the ionic liquid. The relatively higher proportion of methanol in the solvation shell of the reactants “shields” the reaction from the increasing friction, while probably stabilizing the transition state through hydrogen bonding effects.²⁵

The polarity of mixtures of ionic liquids–methanol and ionic liquids–chloroform shows different behavior due to the large polarity difference between methanol and chloroform. In the case of a binary mixture of ionic liquids–methanol, the polarity varies in a synergetic manner, in which the polarity of mixture is higher than those of the pure solvents.²⁵ But in the case of an ionic liquids–chloroform binary mixture, the polarity alters nonideally and is directed by ionic liquids only. The rate constants in an ionic liquids–methanol system decrease nonideally but in a certain composition range remain invariant, because of the synergetic effect. In the ionic liquids–chloroform system, the rate constants do not vary polarity.

c. Ionic Liquid–Water Binary Mixtures. From the plots of rate constants k_2 versus different concentrations of ionic liquids in water shown in Figure 5, it is observed that the rate constants decrease with increase in concentration of ionic liquids in water. The viscosity also increases with increase in concentration of ionic liquid in water. The identity of the ionic liquid does not make an appreciable difference in the observed rate constants, implying that the methyl substituent is distant from the reaction center in the solvated form of the transition state. A similarity between the rate profiles for the three ionic liquid mixtures is much greater in the presence of water as a cosolvent rather than methanol as the other component.

In the highly aqueous region, the rate constants decrease from the $24.82 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for pure water to $5.01 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for $V_{t,2} = 0.2$ of $[\text{BP}][\text{BF}_4]$ ionic liquids and viscosity increases from 0.89 to 1.33 cP. Similarly the rate constants decrease for a binary mixture of $[\text{3-MBP}][\text{BF}_4]$ and $[\text{4-MBP}][\text{BF}_4]$ in water as $24.82 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for pure water to $2.07 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for $V_{t,2} = 0.2$ of ionic liquids in water and $24.82 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for pure water to $2.71 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for $V_{t,2} = 0.2$ of ionic liquids in water, respectively. The corresponding viscosity increases for $[\text{3-MBP}][\text{BF}_4]$ –water mixture from 0.89 to 1.42 cP and for $[\text{4-MBP}][\text{BF}_4]$ –water mixture from 0.89 to 1.40 cP. Beyond this composition, the viscosity

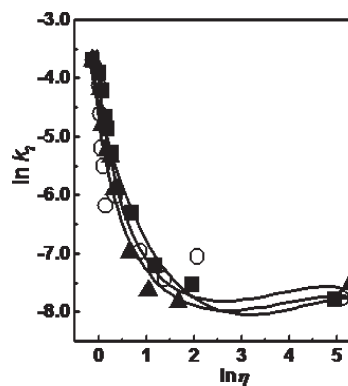


Figure 6. The plots of $\ln k_2 - \ln \eta$ in binary mixtures of $[\text{BP}][\text{BF}_4]$ (■), $[\text{3-MBP}][\text{BF}_4]$ (○), and $[\text{4-MBP}][\text{BF}_4]$ (▲) in water.

change is very high but rate constant does not show much change as compared to the earlier region.

The decrease in rate constants of Diels–Alder reaction with addition ionic liquids to water has been ascribed to three factors: (1) decreased polarity of the transition state in ionic liquids, (2) the antihydrophobic effect of ionic liquids which solvate the organic reactants independently, and (3) diminished hydrogen bonding effects of water in the transition state.³³ From Figure 5, trigger points are the significant points where the exponential rates changed more drastically. The results suggest the presence of additional factors, other than viscosity, in determining the reactivity between **1** and **2**. The difference in the polarity of water and ionic liquid as well as the hydrogen bonding capacity of the water molecule could be the decisive factors, as discussed previously for the binary mixtures of methanol. The high degree of similarity of rate profiles for the different ionic liquids, in addition, indicates an even greater extent of preferential solvation in aqueous systems as compared to methanol binary systems. Earlier reports suggest that the kinetics of organic reaction is drastically accelerated in water due to the hydrophobic effect of water.³⁴ It is difficult to quantify the extent of the hydrophobic effect for the system under study. The dominant role of the hydrophobic effect is, nevertheless, a reasonable explanation for the dramatic increase in reactivity in the highly aqueous region. This hydrophobicity of water decreases with addition of ionic liquids and solvates the reactants more independently, which slow down the diffusion process reaction rate.

At this stage, it is of interest to invoke the effect of pairwise interactions operating in the system. Following the pioneering contribution of Engberts and his school³⁵ on hydrophobic hydration and its use in explaining Diels–Alder reactions in highly aqueous solutions, it is possible to throw light on correlating the reaction rates with the concept of pairwise interactions. Within this framework, the rate effects are discussed in terms of pairwise Gibbs function interaction parameters attributed by the respective interactions of the cosolvent molecules with the initial state and the activated complex of the reaction.

This additivity principle is used to analyze the thermodynamics of solute–solute interactions in aqueous media.³⁵ The linear relationship between $\ln(k_2/k_2^0)$ versus molality of cosolvent shows the presence of pairwise interaction and has been incorporated into a quantitative analysis of kinetic medium effects for highly dilute solutions given by eq 2.

$$\ln \left(\frac{k_2}{k_2^0} \right) = \frac{2}{RT} G(\text{C})m - n\Phi M_1 m \quad (2)$$

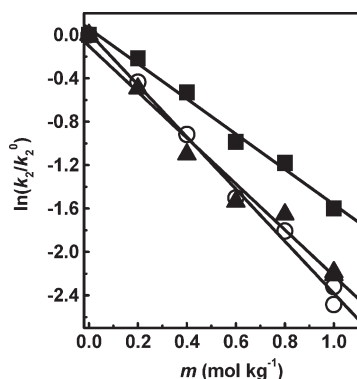


Figure 7. Plots of $\ln(k_2/k_2^0)$ vs m of $[\text{BP}][\text{BF}_4]$ (■), $[\text{3-MBP}][\text{BF}_4]$ (○), and $[\text{4-MBP}][\text{BF}_4]$ (▲) in highly aqueous media at 298.15 K.

Table 1. The $G(C)$ Values for the Diels–Alder Reaction in the Aqueous Solutions of Ionic Liquids at 298.15 K

ionic liquids	$G(C)$, J kg M^{-2}
$[\text{BP}][\text{BF}_4]$	−2010.3
$[\text{3-MBP}][\text{BF}_4]$	−3031.7
$[\text{4-BP}][\text{BF}_4]$	−2629.4

where k_2 is second order rate constant for the Diels–Alder reaction in a binary mixture of ionic liquids in water, k_2^0 is the rate in pure water, m is the molality of cosolvent, n is the number of water molecule involved in activated complex, Φ is the practical osmotic coefficient of water ($\Phi = 1$ for highly aqueous solution), M_1 is the molar mass of water, and $G(C)$ is the difference in Gibbs energy of interaction between the cosolvent and the initial state and the cosolvent and the transition state, respectively. $G(C)$ represents the overall effect of the cosolvent on the Gibbs energy of activation for the Diels–Alder reaction and is obtained from the slope of a linear plot of $\ln(k_2/k_2^0)$ vs molality m of the cosolvent.

The $G(C)$ values calculated for aqueous solutions of $[\text{BP}][\text{BF}_4]$, $[\text{3-MBP}][\text{BF}_4]$, and $[\text{4-MBP}][\text{BF}_4]$ are shown in Table 1. The highly negative values of $G(C)$ designate that the initial state is more stabilized by ionic liquids which did not allow any significant aggregation of the diene and dienophile at concentrations used for the kinetic measurements. The cosolvents stabilize the initial state to a larger extent than the transition state which increases the Gibbs energy of activation leading to a decrease in rate constant. From a comparison with similar types of reactions, it appears that the values of $G(C)$ for ionic liquids are much higher than those for organic solvents. The presence of a methyl group and position of the substituent on cations of ionic liquids also affect the solvation of diene and dienophile.

In addition to this, one of important properties of ionic liquids is surface tension. It has been reported that surface tension of ionic liquids is governed by the anions. Ionic liquids possess a lower surface tension than water and it decreases with the addition of ionic liquids. The decrease of the viscosity of ionic liquids by the addition of cosolvents followed a different pattern depending on the nature of the cosolvents added, possibly due to differences in polarities which led to different interactions with the ions in the ionic liquids.²³ When the ionic liquid concentration increases, the viscosity does not increase a great deal in the dilute solution but increases rapidly in the concentrated solution. The surface tension of ionic liquids in aqueous solution decreases with increase in the concentration of ionic liquids.

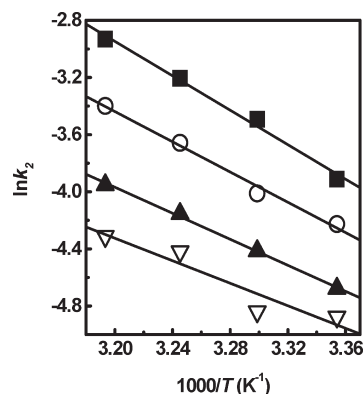


Figure 8. The plots of $\ln k_2 - 1000/T$ for V_{f2} (volume fraction of $[\text{BP}][\text{BF}_4]$ in water) = 0.04 (■), 0.07 (○), 0.11 (▲) and 0.15 (▽) for the binary mixture of $[\text{BP}][\text{BF}_4]$ in water.

Table 2. Activation Parameters for the Diels–Alder Reaction in the Binary Mixtures of Ionic Liquids $[\text{BP}][\text{BF}_4]$ in Water at 298.15 K

S. no.	V_{f2}	$\Delta^\ddagger H$, kJ mol $^{-1}$	$\Delta^\ddagger S$, kJ mol $^{-1}$ K $^{-1}$	$T\Delta^\ddagger S$, kJ mol $^{-1}$	$\Delta^\ddagger G$, kJ mol $^{-1}$
1	0.04	47.63	−0.12	−35.00	82.63
2	0.07	41.48	−0.14	−42.09	83.56
3	0.11	35.29	−0.17	−49.30	84.59
4	0.15	30.22	−0.19	−55.03	85.25
5	0.20	51.41	−0.12	−34.72	86.13
6	0.40	60.76	−0.09	−27.95	88.71
7	0.60	81.71	−0.03	−9.40	91.11

The surface tension of pyridinium based ionic liquids shows 44 $\text{mN}\cdot\text{m}^{-1}$.³⁶ The surface tension of mixture decreased rapidly in dilute solution but almost did not vary in the concentrated solution. The result shows the $[\text{BF}_4]^-$ -based ionic liquids are very active at the surfaces. The ionic liquids decrease the surface tension of water which does not lead to cavity formation in water more easily and solvate the reactants. Hence in highly aqueous medium the change in rate constants, k_2 , is more dramatic as the surface tension, which shows that the surface tension of the medium is the prevailing important role in kinetics of the Diels–Alder reaction.

d. Temperature Dependent Kinetics of the Diels–Alder Reaction. The temperature dependent rate constants k_2 for the Diels–Alder reaction in binary mixtures of $[\text{BP}][\text{BF}_4]$ in water are shown in the form of Arrhenius plots (Figure 8). The plots show that the variation in k_2 for the Diels–Alder reaction in different compositions of highly aqueous region of the binary mixtures of $[\text{BP}][\text{BF}_4]$ –water. The activation parameters for the reaction of 1 with 2 were determined from the temperature dependence of k_2 in $[\text{BP}][\text{BF}_4]$ –water binary mixtures shown in Table 2. The activation parameters enthalpy of activation $\Delta^\ddagger H$, entropy of activation $\Delta^\ddagger S$, and free energy of activation $\Delta^\ddagger G$ were determined for seven different compositions of $[\text{BP}][\text{BF}_4]$ in water. It is seen that the enthalpy of activation, $\Delta^\ddagger H$, decreases from 47.63 to 30.22 kJ mol^{-1} for the concentration of $[\text{BP}][\text{BF}_4]$ in water from $V_{f2} = 0.04$ to $V_{f2} = 0.15$ (Figure 9).

This remarkable behavior may indicate the presence of other factors responsible for the kinetics of the reaction. These values were not in agreement with the qualitative prediction that the

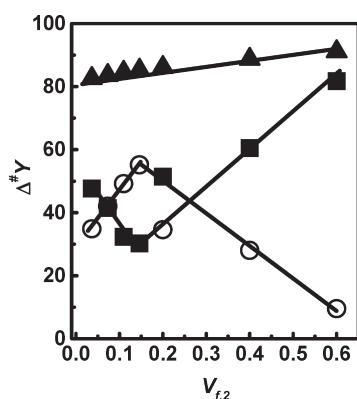


Figure 9. The plots of activation parameters ($\Delta^\ddagger Y$) $\Delta^\ddagger H$ (■), $-T\Delta^\ddagger S$ (○), and $\Delta^\ddagger G$ (▲) for the binary mixtures of [BP][BF₄]-water; units are in kJ mol⁻¹.

reactants will have to overcome a “higher barrier” in a more viscous medium, leading to a decrease in the rate of the reaction. It has been also observed that the entropy of activation might play an important role in the organic reaction which leads to a phenomenon known as *entropy–enthalpy compensation*.

At composition in the highly aqueous region, water becomes even more structured by the formation of hydrophobic hydration shells as seen by numerous spectroscopic studies. As a result, hydrophobic interactions will become entropically slightly more favorable. The term hydrophobic hydration refers to the interactions of apolar solutes and water, i.e., how an apolar solute affects the water structure in its immediate environment. Introduction of an apolar solute into aqueous solution is characterized by an unfavorable change in standard Gibbs energy at room temperature.^{37–39} However, the standard enthalpy of the solution process is usually small and favorable whereas the entropy change is large and negative.^{37–40} The dependence of $\Delta^\ddagger H$ and $T\Delta^\ddagger S$ at 298.15 K for the reaction of **1** with **2** on the mole fraction of [BP][BF₄] in dilute aqueous solutions is dramatic. The changes of $\Delta^\ddagger H$ and $T\Delta^\ddagger S$ across the mole fraction range of $0 < x_2 < 0.15$ are spectacular. The enthalpy of activation decreases upon addition of [BP][BF₄]. Simultaneously, the entropy of activation exhibits an equally dramatic decrease. The effects almost fully compensate each other.^{41–43} Hence in the water-rich media the free energy of activation for the Diels–Alder process is only moderately affected by the addition of ionic liquids to water. The reaction is slowed down by addition of structure-promoting cosolvents. At a critical concentration of water molecules, water gradually loses its typically aqueous character. **1** and **2** will become more and more preferentially solvated by the ionic liquids, and the driving force for the dramatic rate effect in water will be lost. Finally, beyond these concentrations of ionic liquids, where the concentration fluctuations are at their maximum, the binary mixtures start to behave like a common solvent, leading to smooth changes in rate and activation parameters upon variation of the ionic liquids composition.

The unfavorable Gibbs free energy for solution in water is the result of strongly negative entropy of solution which prevails over the favorable enthalpic contribution. The domination of entropy effects is often found for chemical processes in water and in water-rich solutions.^{44,45} It is found that the association process is entropy driven. The plot of enthalpy–entropy compensation for the Diels–Alder reaction of **1** and **2** in [BP][BF₄]-water binary mixture is shown in Figure 10.

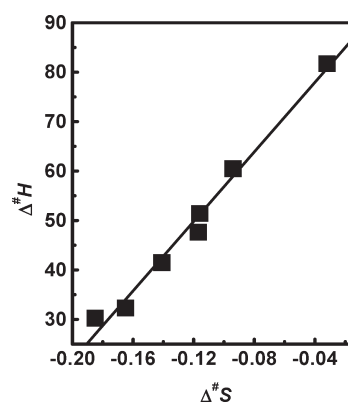


Figure 10. Illustration of enthalpy–entropy compensation plots of $\Delta^\ddagger H$ – $\Delta^\ddagger S$ for the Diels–Alder reaction of **1** and **2**.

Several years ago, one of us had demonstrated an alternate explanation of the rate enhancement in Diels–Alder reactions in water, aqueous salts solutions, and nonaqueous salt solutions with the help of solvent cohesive pressure or CED of solvent systems and the activation volume of the Diels–Alder reactions.⁴⁶ The non-availability of physicochemical data on the ionic liquids solutions restricts our explanation on the above basis.

CONCLUSIONS

The above results show the following:

1. The reactivity in chloroform–ionic liquid binary mixtures is closely related to the viscosity of the reaction medium, indicating the dominance of the frictional forces. For the methanol and water binary mixtures, a more complex correlation is observed wherein the role of viscosity cannot be completely discounted. However, additional solute–solvent interactions dominate the kinetic profile depending on the property of the cosolvent used. A high degree of preferential solvation is certainly responsible for the deviations from ideality observed. In aqueous systems, the presence of hydrophobic forces is observed distinctly.
2. The kinetic data can be interpreted in terms of a pairwise model built upon enforced hydrophobic hydration.
3. The activation parameters for the aqueous binary mixtures showed enthalpy–entropy compensation effects.
4. Most importantly, despite the strong intermolecular forces, the effect of viscosity is a consistently effective feature for all the ionic liquid systems studied. The results point toward the possibilities of manipulating the reactivity of organic compounds by a judicious and well-informed choice of ionic liquid binary systems. It is hoped that the above study will open doors for solvent engineering via the use of physicochemical property, e.g., viscosity of the solvent medium.

ASSOCIATED CONTENT

S Supporting Information. Three tables containing the values of second-order rate constants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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