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Kinetics study of a Diels-Alder reaction in mixtures of an ionic liquid with molecular solvents

Ali Reza Harifi-Mood^a, Aziz Habibi-Yangjeh^b
and Mohammad Reza Gholami^{a*}

The second-order rate constants for cycloaddition reaction of cyclopentadiene with naphthoquinone were determined spectrophotometrically in various compositions of 1-(1-butyl)-3-methylimidazolium tetrafluoroborate ([bmim]BF₄) with water and methanol at 25 °C. Rate constants of the reaction in pure solvents are in the order of water > [bmim]BF₄ > methanol. Rate constants of the reaction decrease sharply with mole fraction of the ionic liquid in aqueous solutions and increase slightly to a maximum in alcoholic mixtures. Multi-parameter correlation of log *k*₂ versus solute-solvent interaction parameters demonstrated that solvophobicity parameter (Sp), hydrogen-bond donor acidity (α) and hydrogen-bond acceptor basicity (β) of media are the main factors influencing the reaction rate constant. The proposed three-parameter model shows that the reaction rate constant increases with Sp, α and β parameters. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: ionic liquid; Diels-Alder; solvent effect

INTRODUCTION

Reactions involving isopolar-activated complexes, such as Diels-Alder (DA) reactions, normally exhibit small solvent effects and, consequently, studies on this topic have traditionally been scarce.^[1] However, interest in the role of the solvent in DA reactions has increased over the last decade because of the noticeable improvement in these reactions achieved by the use of water or aqueous solutions.^[2–7] The fact that rate constants for DA reactions in water are dramatically larger than those in organic solvents contradicts with common notion that DA reactions are rather insensitive to solvent effects.^[7] In addition to obvious economical and environmental advantages, water has surprisingly beneficial effects on organic reactions, which has popularized water as a reaction medium.^[8–11] Chemical reactions can be affected by the solvent through several kinds of interactions. Studies on solvent effects are generally carried out by means of relationships between reactivity properties, that is reaction rate or several types of selectivity, and empirical parameters representing different kinds of solute-solvent interactions.^[7,12–15]

Ionic liquids (ILs) have recently been regarded as an eco-friendly alternative to replace volatile organic solvents in current chemical processing, due to their unique physical and chemical properties.^[16–19] Furthermore, there are wide ranges of cations and anions that have been used in the preparation of ILs, giving a great potential for synthetic variation.^[20,21] ILs seem to be the suitable media for DA reactions and have been used as both solvents and catalysts for such reactions.^[1,22–24] Tiwari and Kumar^[25] have recently shown that ILs are not as effective as water in accelerating DA reaction. Many DA reactions have been studied in this media and the solvent influences on the *endo/exo* selectivity of the reaction are well

understood.^[24] However, a few investigations deal with the ILs media and the solvent effects on chemical kinetics of DA reactions.^[24,26–27]

In continuing our studies on ILs,^[28,29] in the present work, we report a kinetics study of the cycloaddition reaction between cyclopentadiene (**1**) and naphthoquinone (**2**) (Scheme 1). Second-order rate constant of the reaction was determined in various compositions of 1-(1-butyl)-3-methyl imidazolium tetrafluoroborate ([bmim]BF₄), as a well-known IL, with water and methanol at 25 °C and the results were interpreted by various solute-solvent interaction parameters.

EXPERIMENTAL SECTION

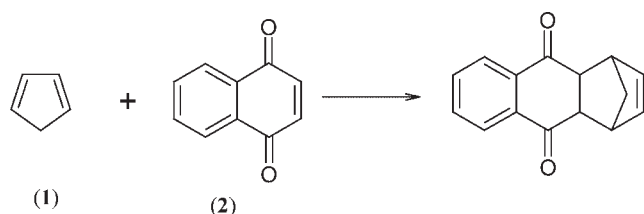
Material

Naphthoquinone (m. p. 126 °C) was obtained from Merck and purified by recrystallization from methanol-light petroleum. Cyclopentadiene, purchased from Merck, was used freshly by distillation of its dimer. Methanol (>99.5%) was supplied by Merck and was used without further purification. Doubly distilled water was used in all solvent samples.

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Scheme 1.

1-(1-Butyl)-3-methylimidazolium tetrafluoroborate (>98%), stored under nitrogen, was purchased from Solvent-Innovation GmbH and was used as received. Karl Fischer titrations showed no detectable water was present in freshly purchased [bmim]BF₄.

Kinetic measurements

In order to check stability, the reactants and product of the reaction were stored in [bmim]BF₄-solvent media for 24 h and did not find any competitive reaction. The kinetics of the reaction was studied spectrophotometrically by running the reaction in the thermostated cells of spectrophotometer at 25 °C. A GBC UV-vis cintra 40 spectrophotometer coupled with a thermocell was used with 1.00 cm silica cells. The absorbance variation with time was recorded at $\lambda = 330\text{--}340$ nm for naphthoquinone of the reaction regarding to composition of media. The reaction rate is slow; therefore, the kinetics of reactions was studied under pseudo-first-order conditions and initial rate method. However, in water-rich regions, the reaction rate is fast enough to use the rate-integrated method.

RESULTS AND DISCUSSION

The second-order rate constants of the cycloaddition reaction between cyclopentadiene (1) and naphthoquinone (2) in various compositions of [bmim]BF₄ with water and methanol were determined at 25 °C (Tables 1 and 2).

Several main types of parameters representing solute–solvent interactions, such as dipolarity/polarizability parameter (π^*), hydrogen-bond donor acidity (α), hydrogen-bond acceptor

Table 1. Second-order rate constants of the reaction between (1) and (2) in water–[bmim]BF₄ mixtures at 25 °C

x_{IL}	$10^2 \times k_2/\text{M}^{-1} \text{s}^{-1}$	E_T^N	α	β	π^*
0	415 ± 8	1.00	1.3	0.46	1.1
0.05	85.7 ± 0.9	0.91	1.12	0.55	1.06
0.1	34.3 ± 0.8	0.84	1.0	0.6	1.03
0.2	15.9 ± 0.6	0.81	0.95	0.62	0.99
0.3	9.79 ± 0.14	0.78	0.91	0.6	0.99
0.4	7.34 ± 0.11	0.76	0.89	0.59	0.96
0.5	4.90 ± 0.12	0.75	0.86	0.57	0.96
0.6	3.67 ± 0.08	0.75	0.85	0.56	0.96
0.7	3.40 ± 0.09	0.73	0.81	0.54	0.96
0.8	2.86 ± 0.09	0.73	0.82	0.54	0.95
0.9	2.37 ± 0.11	0.75	0.87	0.53	0.94
1	2.05 ± 0.13	0.67	0.75	0.59	0.89

Table 2. Second-order rate constants of the reaction between (1) and (2) in methanol–[bmim]BF₄ mixtures at 25 °C

x_{IL}	$10^2 \times k_2/\text{M}^{-1} \text{s}^{-1}$	E_T^N	α	β	π^*
0.0	1.95 ± 0.04	0.76	1.16	0.8	0.58
0.1	2.33 ± 0.03	0.83	1.15	0.68	0.79
0.2	2.34 ± 0.03	0.83	1.1	0.63	0.85
0.3	2.32 ± 0.04	0.82	1.06	0.6	0.88
0.4	2.25 ± 0.04	0.81	1.03	0.57	0.91
0.5	2.19 ± 0.03	0.8	0.99	0.55	0.93
0.6	2.16 ± 0.05	0.79	0.96	0.55	0.93
0.7	2.11 ± 0.07	0.77	0.92	0.54	0.93
0.8	2.07 ± 0.07	0.76	0.9	0.54	0.93
0.9	2.06 ± 0.08	0.75	0.87	0.53	0.94
1.0	2.05 ± 0.13	0.67	0.75	0.59	0.89

basicity (β), normalized polarity parameter (E_T^N) and solvophobicity parameter (S_p) have been proposed in order to explain the variations in rate of the reactions by modifying the reaction media. The solvatochromic parameters for solutions of [bmim]BF₄ with water and methanol at various compositions have been determined in our laboratory (Tables 1 and 2).^[29]

The rate constants in mixtures of methanol and water with [bmim]BF₄ follow different patterns. A nonlinear dependence of k_2 on the mole fraction of IL is observed. This behaviour is attributed to preferential solvation effects. In alcoholic solutions, rate constants have a maximum in alcohol-rich region while the rate constant is moderately invariant in IL-rich area. Since, the dienophile is capable of accepting hydrogen bonds, the variation of rate constant with IL as cosolvent may cause change in hydrogen bond abilities and polarity of media, we have proved that hydrogen bond acceptor/donor abilities and dipolarity/polarizability have been demonstrated synergism.^[29] This behaviour is attributed to a hydrogen bond interaction between IL and alcohol to give hydrogen-bonded complex in the media, which is more polar and a better hydrogen bond donor (HBD) than the two constituents of the mixture.^[30] Of course, variation of the reaction is moderate and this makes a reliable interpretation of these small effects extremely difficult; however, it can be a good example of different solvent effects compare with the aqueous solutions.

Many papers referred that imidazolium-based ILs show polarity like short chain alcohols.^[29,31–36] Thus, the rate constant value of the reaction in pure IL, which is near to its value in pure methanol, reflects the influence of the polarity on the reaction rate as only one of the effective solvent parameters in this reaction.

In aqueous solution, the rate constant reduces sharply with IL content. Solvent polarity, hydrogen bonding and enforced hydrophobic interactions are important factors that may affect the rate constant. The absence of hydrophobic interactions and weaker hydrogen bonding in ILs may be the important reasons for the observed difference in the rates between water and ILs. For example, the HBD ability in water is approximately twice that in [bmim]BF₄.^[29] The rate constant of DA reaction carried out in different ILs have been correlated with the $E_T(30)$ parameter.^[25] Since $E_T(30)$ parameter has correlation with H-bonding ability, the rate constant of these reactions decreases with the decrease in HBD ability of ILs.

Table 3. S_p values in water–[bmim]BF₄ and methanol–[bmim]BF₄ mixtures

x_{IL}	S_p in water– [bmim]BF ₄ system	S_p in methanol– [bmim]BF ₄ system
0	1	0.1998
0.05	0.7981	—
0.1	0.6935	0.2755
0.2	0.5874	0.3198
0.3	0.5264	0.3488
0.4	0.5026	0.3691
0.5	0.4717	0.3846
0.6	0.4686	0.3961
0.7	0.4579	0.4058
0.8	0.4473	0.4125
0.9	0.4366	0.4192
1	0.4259	0.4259

Correlation with the composition of the media

In order to observe the solvent effects on the reaction, single and multi-parameter correlation between $\log k_2$ and parameters of solvent was investigated. We have attempted to rationalize the observed trends in rate constants of the reaction in terms of solvophobicity parameter, normalized polarity parameter or Abraham–Kamlet–Taft (AKT) parameters including π^* , α and β . For all mixtures, values of E_T^N , α , β and π^* are available.^[29] Values of S_p for the pure IL were calculated based on the Abraham method^[37] and solubility data for rare gases and alkanes in [bmim]BF₄ are also demonstrated (Table 3).^[38] Values of S_p for many binary mixtures give a fair linear correlation with the volume fraction of constituents.^[15,37] Thus, we have estimated the S_p values for water–[bmim]BF₄ and methanol–[bmim]BF₄ mixtures by the following equation:

$$S_p = f_1 S_{p1} + (1 - f_1) S_{p2} \quad (1)$$

where f_1 is the volume fraction of [bmim]BF₄ and S_{p1} and S_{p2} are solvophobicity parameter in pure [bmim]BF₄ and water (or methanol), respectively. The S_p values of the corresponding mole fractions and values between those listed for mixtures of [bmim]BF₄ and water were linearly interpolated and have been summarized in Table 3 and plotted in Fig. 1.

In order to suggest a complete and reasonable model for solvent effects on this reaction, mixtures of solvents were separately investigated.

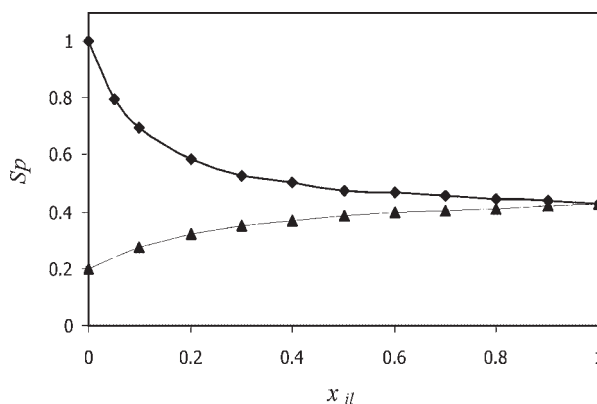
Water–[bmim]BF₄ system

Single-parameter correlation of $\log k_2$ values versus E_T^N in water–[bmim]BF₄ mixtures gives an acceptable result (Eqn (2)).

$$\log k_2 = -7.015 (\pm 0.283) + 7.646 (\pm 0.357) E_T^N \quad (2)$$

$n=12, r=0.989, s=0.108, F_{1,10}=459.38$

where n , r , s and F are the number of data, regression coefficient, standard error and statistical Fisher number, respectively. As can be seen, the second-order rate constant of the reaction increases with the increasing normalized polarity parameter. Figure 2

**Figure 1.** Variation of the solvophobicity of water–[bmim]BF₄ (◆) and methanol–[bmim]BF₄ (▲) mixtures with mole fraction of [bmim]BF₄

shows a good correlation of the calculated $\log k_2$ by Eqn (2) with the experimental values. Changes in solute–solvent interactions during the activation process will influence the rate constant. Reactions, which are accompanied by an increase in the charge separation in their activation process, are accelerated in solvents of increasing polarity. Thus, increasing the reaction rate constant is attributed to a major interaction of the polar media with the activated complex relative to the reactants. Similar results have been reported in molecular solvents.^[2–4,37] In addition, the solvent would destabilize the reactants through its solvophobicity parameter because in the reaction of two apolar reactants, the unfavourable water contacts with reactants are reduced and then the apolar reactants have a tendency to stick together in aqueous solutions. Therefore, solvophobicity parameter is one of the factors that affect the reaction rate constant. It can be seen that the rate constants have a fair correlation with solvophobicity of the media (Eqn 3).

$$\log k_2 = -3.239 (\pm 0.103) + 3.954 (\pm 0.174) S_p \quad (3)$$

$n=12, r=0.990, s=0.102, F_{1,10}=517.87$

Obviously the reaction rate constant increases with the increasing solvophobicity parameter. This equation shows that hydrophobic effects only play a role in aqueous solutions and demonstrates the better correlation with $\log k_2$ than the normalized polarity (Fig. 3). Therefore, the normalized polarity parameter and solvophobicity parameter of the media are not individually the main factor in determining solvent effects on the reaction rate. Merging these effects in one equation produces a good correlation as dual-parameter regression of $\log k_2$ versus E_T^N and S_p (Eqn (4)).

$$\log k_2 = -5.021 (\pm 0.793) + 3.572 (\pm 1.580) E_T^N + 2.139 (\pm 0.816) S_p \quad (4)$$

$n=12, r=0.994, s=0.086, F_{2,9}=367.85$

where standardized coefficients for E_T^N and S_p are 0.536 and 0.462, respectively. As can be seen, E_T^N and S_p have approximately equal effects on increasing the reaction rate in aqueous solution of [bmim]BF₄. In order to show efficiency of the suggested dual-parameter equation, the calculated values of the reaction rate constant in mixtures of water with [bmim]BF₄ using Eqn (4) have been plotted versus the experimental values. Figure 4

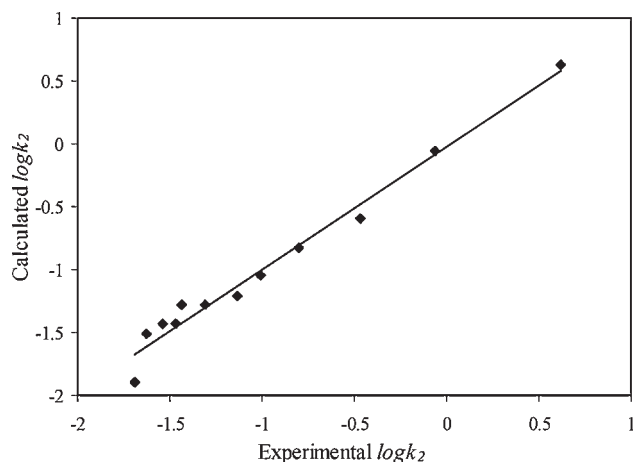


Figure 2. Plot of the calculated values, by Eqn (2), versus the experimental values of $\log k_2$ in aqueous solutions of [bmim]BF₄

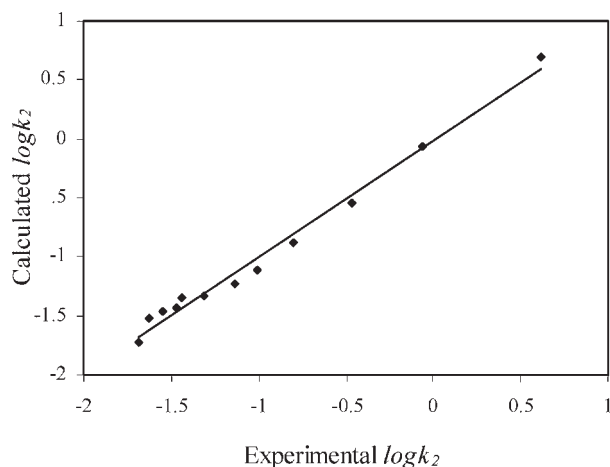


Figure 4. Plot of the calculated values, by Eqn (4), versus the experimental values of $\log k_2$ in aqueous solutions of [bmim]BF₄

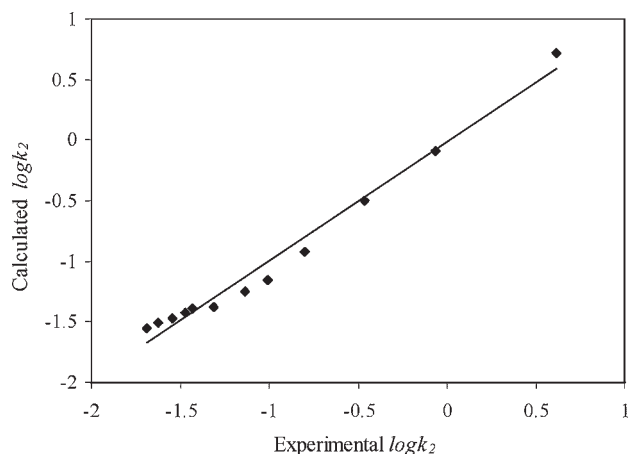


Figure 3. Plot of the calculated values, by Eqn (3), versus the experimental values of $\log k_2$ in aqueous solutions of [bmim]BF₄

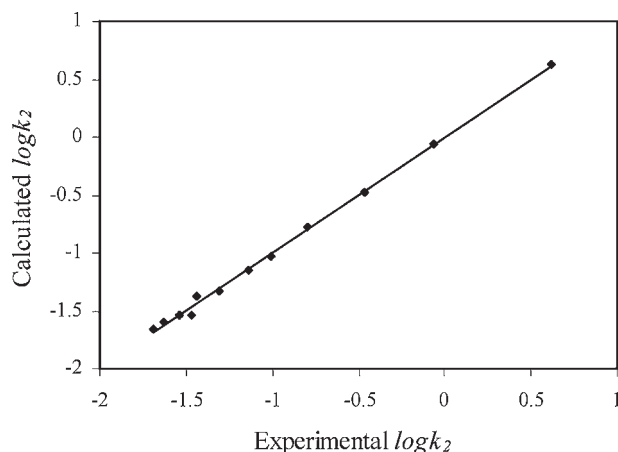


Figure 5. Plot of the calculated values, by Eqn (5), versus the experimental values of $\log k_2$ in aqueous solutions of [bmim]BF₄

demonstrates a good agreement between the experimental and the calculated values of $\log k_2$.

The normalized polarity parameter is a blend of dipolarity/polarizability and hydrogen-bond donor acidity of the media. The main advantage of single-parameter correlations versus E_T^N is its simplicity and a major drawback is that correlations are still difficult to interpret. The multi-parameter approach in terms of AKT models produces acceptable models in which the influence of every parameter on the reaction rate has been illustrated. Thus, multi-parameter correlations of $\log k_2$ versus α , π^* , β and Sp were considered and the following equation was obtained:

$$\log k_2 = -5.548 (\pm 0.298) + 2.569 (\pm 0.511) \alpha + 1.915 (\pm 0.304) \beta + 1.950 (\pm 0.448) \text{Sp} \quad (5)$$

$$n=12, r=0.999, s=0.038, F_{3,8}=1249.90$$

It is clear that the reaction rate constant increases with α , β and Sp values. The standardized coefficients are 0.563, 0.117 and 0.488 for α , β , and Sp, respectively. These coefficients demonstrate that α and Sp parameters are more effective than the β on

the reaction rate. This reaction is an example of a typical DA reaction, in which the dienophile is capable of accepting hydrogen bonds, that promotes the rate of the reaction. Hydrogen-bonding interactions of media (donor and acceptor) with the charges on the activated complex stabilize the activated complex more than the reactant of the reaction. Thus, the reaction rate constant increases with hydrogen-bond donor and acceptor parameters. Figure 5 shows the ability of predicting the rate constants by recent equation.

Methanol-[bmim]BF₄ system

In spite of similar trend between $\log k_2$ and E_T^N , single-parameter correlation of $\log k_2$ versus E_T^N do not give reasonable result in methanol-[bmim]BF₄ solutions ($r=0.784$). Multi-parameter correlation were considered for methanol-[bmim]BF₄ system. Unlike water-[bmim]BF₄ system, dual-parameter regression of $\log k_2$ values versus E_T^N and Sp don't indicate any fair correlation. The consideration of the hydrogen-bond acceptor basicity of the media can produce a better fit compared with the

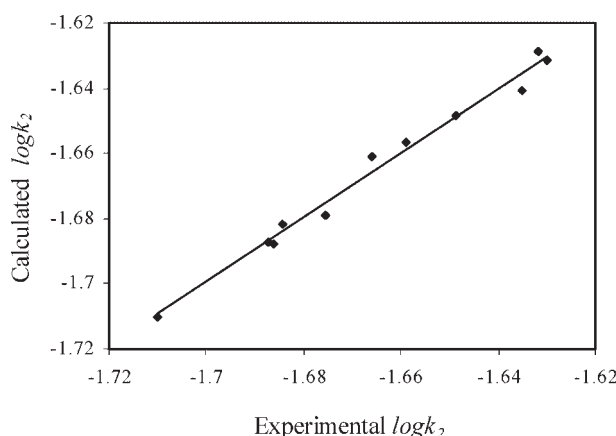


Figure 6. Plot of the calculated values, by Eqn (6), versus the experimental values of $\log k_2$ in mixtures of methanol with [bmim]BF₄

dual-parameter regression (Eqn (6)).

$$\log k_2 = -4.462 (\pm 0.462) + 1.377 (\pm 0.180) E_T^N + 1.613 (\pm 0.313) \beta + 2.103 (\pm 0.390) \text{Sp} \quad (6)$$

$n=11, r=0.966, s=0.008, F_{3,7}=32.713$

Also, this model can be modified by removing the normalized polarity parameter and investigating the dipolarity/polarizability and hydrogen-bond donor acidity of media. There is a reasonable correlation between $\log k_2$ and the three empirical parameters including α , β and π^* (Eqn (7)).

$$\log k_2 = -3.453 (\pm 0.111) + 0.147 (\pm 0.013) \alpha + 1.189 (\pm 0.095) \beta + 1.072 (\pm 0.068) \pi^* \quad (7)$$

$n=11, r=0.994, s=0.004, F_{3,7}=181.05$

The standardized coefficients are 0.702, 3.637 and 4.300 for α , β and π^* , respectively. These coefficients demonstrate that the influence of hydrogen-bond donor acidity of media on the reaction rate is negligible. On the other hand, β and π^* of media have approximately equal effects on the reaction rate. The α parameter demonstrates a trend with a maximum, however in the β trend, a minimum is observed. Summation of these effects shows a synergetic effect on the reaction rate with a maximum around mole fraction of 0.1 for [bmim]BF₄. Figure 6 shows a good agreement between the experimental and the calculated values of $\log k_2$ in the mixtures of methanol with [bmim]BF₄.

Because of small changes in the rate constants in these media, a simple model has not been obtained. Since, it can be a good example to compare the solvent effects in alcoholic solutions with aqueous solutions.

All mixtures

Single-parameter regression of the reaction rate constants with the normalized polarity parameter does not demonstrate good correlation in all solutions ($r=0.777$). Similar to water–[bmim]BF₄ system, introducing solvophobicity parameter into the model shows a better correlation (Eqn (8)).

$$\log k_2 = -4.497 (\pm 0.416) + 2.429 (\pm 0.607) E_T^N + 2.724 (\pm 0.240) \text{Sp} \quad (8)$$

$n=22, r=0.974, s=0.146, F_{2,19}=176.76$

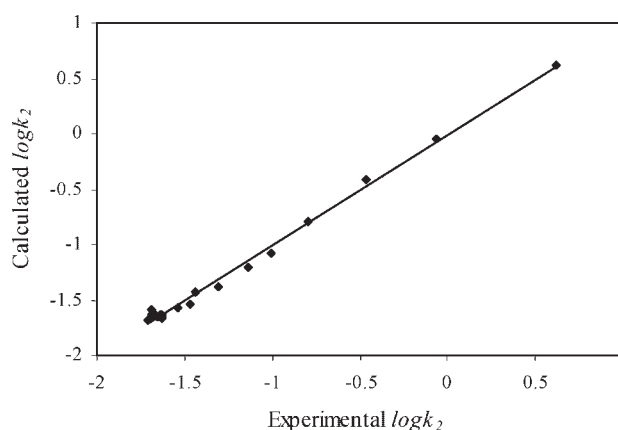


Figure 7. Plot of the calculated values, by Eqn (9), versus the experimental values of $\log k_2$ in all mixtures of the [bmim]BF₄

where standardized coefficients are 0.273 and 0.774 for E_T^N and Sp, respectively. It is clear that solvophobicity of the media has main effect on controlling the reaction rate in the mixtures. Substitution of the normalized polarity parameter with π^* and α parameters and modification of the model confirms a fair correlation of $\log k_2$ with α , β and Sp as shown in Eqn (9):

$$\log k_2 = -4.919 (\pm 0.133) + 0.681 (\pm 0.092) \alpha + 2.143 (\pm 0.223) \beta + 3.664 (\pm 0.085) \text{Sp} \quad (9)$$

$n=22, r=0.997, s=0.049, F_{3,17}=1118.12$

The standardized coefficients are 0.154, 0.232 and 1.041 for α , β and Sp, respectively. Figure 7 shows the ability of the model for prediction of the reaction rate constant using Eqn (9). This equation also confirms the importance of the solvophobicity parameter in the reaction rate. As can be seen, the experimental and calculated values of $\log k_2$ are in good agreement for all solutions.

Because of large changes in the rate constants in water–[bmim]BF₄ relative to methanol–[bmim]BF₄ media, aqueous solutions play a major role in the modelling of the system (Eqns (8) and (9) are similar to Eqns (4) and (5)). As a result, we suggest that the increase in the reaction rate in the solutions can be attributed to two factors: stabilization of the activated complex of the reaction relative to the reactants owing to the hydrogen-bonding interactions (donor and acceptor) of the media, and a substantial decrease in the hydrophobic surface area of the reactants during the activation process or enforced hydrophobic interactions that destabilize the reactants relative to the activated complex. The obtained results in the mixture of [bmim]BF₄ with water and methanol as aqueous and alcoholic media are similar to the previous studies in molecular solvent,^[2–7] and it proves that the rate of DA reactions is mainly resulted in a combination of hydrophobic and hydrogen-bonding interactions. Thus, unlike what has been reported in a few papers,^[39,40] results indicate that the solvent effects in mixtures of the IL with conventional molecular solvents can be described by means of the solute–solvent interactions. As a result, in continuing our studies,^[28,29] it is obvious that [bmim]BF₄ behaves like methanol or water as a molecular solvent and not as a salt in the reactions.^[41]

CONCLUSIONS

Changes in the solvent composition in presence of [bmim]BF₄, as an IL, demonstrated dramatic effect on the Diels-Alder reaction between cyclopentadiene (**1**) and naphthoquinone (**2**) in aqueous solutions and mild effect in methanolic solutions. Second-order rate constants of the reaction represent a fall off with mole fraction of [bmim]BF₄ in aqueous solutions, but it shows a mild increase with a maximum in solutions of [bmim]BF₄ with methanol. Multi-parameter correlation of log *k*₂ versus solute-solvent interaction parameters shows that hydrogen-bond donor acidity and solvophobicity of the media have important effect in determining the reaction rate constant in aqueous solutions. Despite of the small changes in the rate constants in the mixtures of methanol with [bmim]BF₄, only with a maximum in alcohol-rich region, three-parameter regression can explain the reaction rate. The hydrogen-bond donor acidity, dipolarity/polarizability and hydrogen-bond acceptor basicity of media have parallel effects on the rate constants. As a result, we can conclude that solute-solvent interaction parameters can describe solvent effects on a typical Diels-Alder reaction rate constant and the behaviour of [bmim]BF₄ as a solvent can be described such as conventional molecular solvents in the solvent mixtures.

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