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Iso-solvation effects in mixtures of ionic liquids on the kinetics of a model S_NAr reaction†

J. Alarcón-Espósito, *^a R. Contreras^a and P. R. Campodónico*^b

The S_NAr reaction between 1-chloro-2,4-dinitrobenzene and morpholine was used as a model system to study solvation effects in a series of mixtures involving imidazolium based ionic liquids. Iso-solvation regimes (i.e. a solvent composition regime where the solute is being solvated by approximately the same number of different solvent molecules in the mixture) are reported for the first time in ionic liquid mixtures, for 4 mixtures including [EMIM][SCN][DCN], [BMIM][DCN][BF₄], [BMIM][BF₄][PF₆] and [BMIM][PF₆][FAP]. The results show that for significant changes in composition, the rate coefficients remain approximately constant. An additional interesting result is that the mixture [BMIM][BF₄][PF₆] (in the proportion of 0.9 for the molar fraction of BMIMBF₄) shows a slightly better kinetic performance as compared to pure BMIMBF₄ and BMIMPF₆. Finally, for the [EMIM][SCN][DCN] mixture, an increasing proportion of EMIMSCN with respect to EMIMDCN results in a decrease in the rate coefficient within the range of (0.1–0.75) for the molar fraction of EMIMSCN. This result may be traced to competition between the anions [SCN[−]] and [DCN[−]] towards the reaction center driven by the basicity of the reaction medium.

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Introduction

The use of solvent conventional mixtures has largely been documented in the literature.^{1–5} These studies have been extended to mixtures involving conventional solvents/ionic liquids^{6–10} and mixtures of ionic liquids.^{11–14} Apart from the solvating properties of these systems, most of these studies are focused on the kinetic responses of several systems. These studies are based mainly on the physico-chemical properties of the mixtures, namely, polarity, ability to form hydrogen bonds (HBs), density, melting point, and viscosity, among others. However, there are few studies of solvent effects in mixtures evaluated against the reaction rate, in order to establish their usefulness in possible catalytic effects exerted by the solvent mixture.^{15–17} The main difficulty in mixtures of ionic liquids (ILs) is that the problem implies a three-body problem. Remember that ILs are generally associated to a very low extent¹⁸ and therefore one has to lead with interactions between the substrate and a non-associated cation/anion pair.¹⁹ Note also that in the case of ILs, the solvent–solvent interactions also play a significant role. This interaction is normally neglected in neutral dipolar solvents. One way to facilitate the study is to leave one of the components fixed with respect to the counterions. In this study, the cation of the ILs was fixed, since there are antecedents

for the reaction under study, pointing to predominant “anion” solvent effects.²⁰

For instance, Rogers *et al.*²¹ studied the properties of IL mixtures as reaction media using H¹ and C¹³ NMR and IR techniques. The study was based on mixtures of two ILs carrying the common cation [EMIM⁺] with two different anions [OAc[−]] and [NTF₂[−]], to investigate specific solvation effects. These authors demonstrated that the electrostatic interactions are very different from those produced in pure ILs with respect to their mixtures, thereby attributing this response to the ability of [OAc[−]] to form complexes with [EMIM⁺] closest to the other anion [NTF₂[−]]. This effect was related to effects of basicity and the strength of coulombic forces leading to high ordered lattices governed by the nature of the cation/anion. Another determining factor can be, to a lesser extent, the length and steric hindrance of the substituents in the ions. This result agrees well with those obtained in a previous work by our group, regarding the importance of the size, polarizability and ability to form a HB of the anions (which is normally related to their Lewis basicity).^{20,22}

D’Anna *et al.*²³ have proposed that the three-dimensional organization in IL mixtures is important, because this packing defines different domains (micro-environments). These authors studied the rate constant of a Diels–Alder reaction, finding that in those IL mixtures that differ only in the size of the anions, there appear structural variations large enough to compensate the effect of the viscosity of the mixtures, and consequently the kinetic results mainly correspond to the difference in the structural organization induced by the medium, thereby emphasizing that the effect of IL mixtures is strongly substrate-dependent.

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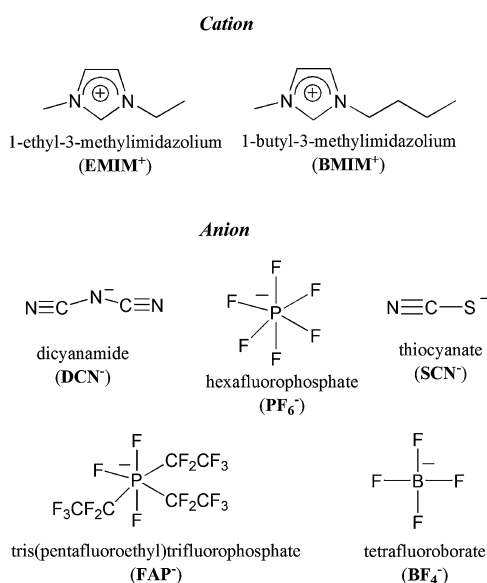
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7nj03246c

Kirchner *et al.*²⁴ performed a combined theoretical–experimental study, based on molecular dynamics, to simulate the environment in mixtures of ILs with respect to pure ILs. Complementing this with an NMR study, they investigated changes in chemical shifts of hydrogen atoms due to the competition of the ions for the same sites of interaction. This fact is reflected differently in the various physicochemical properties, therefore, they concluded that IL mixtures can be both “ideal” and “non-ideal” depending on the properties examined and the reaction under study.

In this work, we will study solvation in IL mixtures from a kinetic point of view, using the Kamlet–Taft solvation model^{25–27} with the objective of obtaining additional information about the specific interactions, namely HB, ion–ion and ion–dipole interactions that would be affecting the kinetics of the model reaction. The chosen ILs were selected from a series of ILs used in a previous work²⁰ in which the same reaction was studied in pure ILs (see Scheme 1), with the aim of analysing any additional information that could be present with reference to the mixture. Scheme 1 summarizes the series of ILs used in this study.

The aim of this study is to look for catalytic processes, if any, in which the values of the kinetic constant are higher than those reported for pure ILs. It should be emphasized that the analysis of the solvent effect is largely more complex because the repulsion forces between the solvent molecules, specifically the anions in this case, preclude a clean analysis of the solute–solvent interaction. However, based on the experimental results found, it is possible to observe zones of iso-solvation. The effects of iso-solvation have been extensively studied in conventional solvent mixtures.^{28–30} Specifically in inorganic chemistry, through ion in solution studies using NMR techniques,³¹ relating the donor or acceptor capacities of the solvent mixtures with respect to the pure solvents.³²

The concept of iso-solvation has been introduced to indicate the composition of a mixture in which the probe under



Scheme 1 Cation/anion structures used in this study.

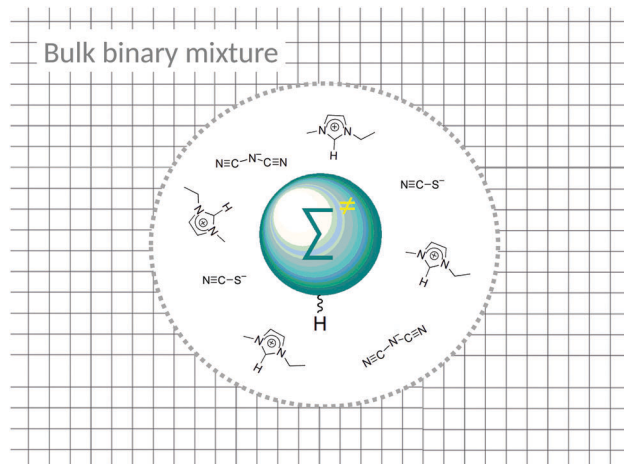


Fig. 1 Schematic representation of iso-solvation for a hypothetical mixture of [EMIM]/[SCN][DCN]. The scheme represents “the first” sphere of solvation in the mixture, where the probe Σ represents the activated substrate.

consideration is solvated by an approximately equal number of co-solvent molecules in the solvent mixture. A schematic model of iso-solvation is illustrated in Fig. 1.

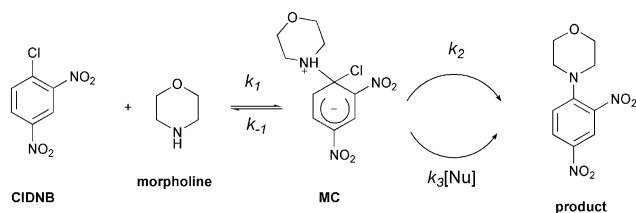
Results and discussion

The studied reaction follows an aromatic nucleophilic substitution (S_NAr) pathway under experimental conditions of pseudo first order. S_NAr is a stepwise mechanism, where the first step leads to the formation of a zwitterionic complex named the Meisenheimer Complex (MC) from which two processes for its decomposition have been postulated: (i) expulsion of the leaving group (LG: $-Cl$) followed by the fast proton loss to give the reaction product and (ii) the base-catalysed deprotonation of the MC that loses the LG to give the reaction product.^{33,34} Under the experimental conditions used only one kinetic product was spectrophotometrically observed for all the reactions studied. See Scheme 2.

The kinetic analysis shows that the pseudo first order rate constant (k_{obs}) for all the study can be expressed as eqn (1), in which $[Nu]$ represents the concentration of the nucleophile (morpholine).

$$k_{obs} = \frac{(k_1 k_2 [Nu] + k_2 k_3 [Nu]^2)}{k_1 + k_2 + k_3 [Nu]} \quad (1)$$

The k_{obs} values were obtained at different concentrations of the nucleophile $[Nu]$ in each reaction media. These results were



Scheme 2 General mechanism for a S_NAr reaction between morpholine as a nucleophile (Nu) towards 1-chloro-2,4-dinitrobenzene as the electrophile.

plotted through k_{obs} vs. $[\text{Nu}]$ in order to obtain the nucleophilic attack rate constant (k_N) values from eqn (2).

$$k_{\text{obs}} = k_0 + k_N[\text{Nu}] \quad (2)$$

Then the k_{obs} values can be expressed like eqn (3), where k_N is determined from the slope of the linear plots, where $k_{-1} + k_2 \gg k_3[\text{Nu}]$:

$$k_{\text{obs}} = k_N[\text{Nu}] \text{ and } k_N = \frac{k_1 k_2}{k_{-1} + k_2} \quad (3)$$

We first performed a complete kinetic study of the model reaction in different IL binary mixtures at 25 °C, keeping the imidazole cation fixed and performing a systematic variation of the compensating anion, according to the following characteristics: (i) ability to form a hydrogen bond; (ii) significant differences in the kinetic constant (k_N) relative to pure ILs; (iii) anion size; (iv) anion coordination; (v) substituents present in the anion, among others. Table 1 compiles the kinetic information obtained from the reaction between 1-chloro-2,4-dinitrobenzene (CIDNB) and morpholine in a series of binary mixtures, organized by families based on the cation imidazolium (EMIM⁺ and BMIM⁺) with different anions (see Scheme 1). To identify the composition of each of the mixtures, the following nomenclature was used: [cation][anion-IL₁]_a[anion-IL₂]_b, where the subscripts *a* and *b* represent the molar fractions of each IL participating in the mixture.

The most important observations after inspection of Table 1 are as follows: (i) in Family I, if we compare both ILs separately (*i.e.* pure IL), the k_N values in BMIMPF₆ are higher than those in BMIMFAP; both anions present a similar coordination number (see Scheme 1), with a central phosphorus atom, and structurally different substituents. [FAP⁻] shows more ramifications, and therefore, for the type of reaction under study, the effects of steric hindrance by the anion are expected to be significant. Note that this effect is reflected in the k_N values for the mixtures in the composition range {0.1–0.75} for the [BMIM][PF₆] mole fraction. Another important aspect to be highlighted is with respect to the basicity of the pure IL, where the greater basicity of the solvent is attributed to a higher value of k_N in agreement with the results obtained from the β parameter of Kamlet and Taft for the pure IL ($\beta_{\text{BMIMPF}_6} = 0.30$ vs. $\beta_{\text{BMIMFAP}} = 0.15$).

(ii) If we now separate Family I and compare it with respect to the IL that has the highest rate constant (BMIMDCN) as a reference, we obtain Families II and III. We can see that the effects of the anion size predominate again because [DCN⁻] is smaller than [PF₆⁻] and [FAP⁻] and more basic than both ($\beta_{\text{BMIMDCN}} = 0.68$) (see Fig. S16 in the ESI[†]). Therefore, it is expected that as the molar fraction (*X*) of [DCN⁻] increases, the values of k_N also increase, in agreement with the kinetic data shown in Table 1 (see Fig. 2).

(iii) For Family IV, the cation changes to [EMIM⁺] this time. Both ILs separately (EMIMSCN and EMIMDCN) have different values of k_N , where EMIMSCN is better kinetically speaking than EMIMDCN (approximately 1.5 times). The interesting point about this Family is that the response is totally different to that expected with respect to the Families I–III previously analysed.

Table 1 Rate constant values (k_N) for the reaction of morpholine with CIDNB in different mixtures of ionic liquids

Family	Mixture LI-LI in molar fractions	k_N 25 °C
I	[BMIM][PF ₆] ₀ [FAP] ₁	0.020 ± 10 ⁻⁴
I	[BMIM][PF ₆] _{0.1} [FAP] _{0.9}	0.027 ± 0.002
I	[BMIM][PF ₆] _{0.25} [FAP] _{0.75}	0.027 ± 0.001
I	[BMIM][PF ₆] _{0.5} [FAP] _{0.5}	0.040 ± 0.002
I	[BMIM][PF ₆] _{0.75} [FAP] _{0.25}	0.050 ± 0.005
I	[BMIM][PF ₆] ₁ [FAP] ₀	0.090 ± 0.001
II	[BMIM][DCN] ₀ [PF ₆] ₁	0.090 ± 0.001
II	[BMIM][DCN] _{0.1} [PF ₆] _{0.9}	0.115 ± 0.006
II	[BMIM][DCN] _{0.25} [PF ₆] _{0.75}	0.109 ± 0.008
II	[BMIM][DCN] _{0.5} [PF ₆] _{0.5}	0.218 ± 0.011
II	[BMIM][DCN] _{0.75} [PF ₆] _{0.25}	0.281 ± 0.021
II	[BMIM][DCN] ₁ [PF ₆] ₀	0.470 ± 0.010
III	[BMIM][DCN] ₀ [FAP] ₁	0.020 ± 10 ⁻⁴
III	[BMIM][DCN] _{0.1} [FAP] _{0.9}	0.031 ± 0.002
III	[BMIM][DCN] _{0.25} [FAP] _{0.75}	0.051 ± 0.003
III	[BMIM][DCN] _{0.5} [FAP] _{0.5}	0.128 ± 0.004
III	[BMIM][DCN] _{0.75} [FAP] _{0.25}	0.198 ± 0.007
III	[BMIM][DCN] ₁ [FAP] ₀	0.470 ± 0.010
IV	[EMIM][SCN] ₀ [DCN] ₁	0.290 ± 0.010
IV	[EMIM][SCN] _{0.1} [DCN] _{0.9}	0.236 ± 0.011
IV	[EMIM][SCN] _{0.25} [DCN] _{0.75}	0.225 ± 0.013
IV	[EMIM][SCN] _{0.5} [DCN] _{0.5}	0.193 ± 0.008
IV	[EMIM][SCN] _{0.6} [DCN] _{0.4}	0.194 ± 0.014
IV	[EMIM][SCN] _{0.75} [DCN] _{0.25}	0.137 ± 0.007
IV	[EMIM][SCN] _{0.9} [DCN] _{0.1}	0.376 ± 0.023
IV	[EMIM][SCN] ₁ [DCN] ₀	0.440 ± 0.020
V	[BMIM][DCN] ₀ [BF ₄] ₁	0.120 ± 0.010
V	[BMIM][DCN] _{0.1} [BF ₄] _{0.9}	0.164 ± 0.005
V	[BMIM][DCN] _{0.25} [BF ₄] _{0.75}	0.278 ± 0.021
V	[BMIM][DCN] _{0.5} [BF ₄] _{0.5}	0.294 ± 0.028
V	[BMIM][DCN] _{0.75} [BF ₄] _{0.25}	0.278 ± 0.019
V	[BMIM][DCN] ₁ [BF ₄] ₀	0.470 ± 0.010
VI	[BMIM][BF ₄] ₀ [PF ₆] ₁	0.090 ± 0.001
VI	[BMIM][BF ₄] _{0.1} [PF ₆] _{0.9}	0.068 ± 0.006
VI	[BMIM][BF ₄] _{0.25} [PF ₆] _{0.75}	0.116 ± 0.009
VI	[BMIM][BF ₄] _{0.5} [PF ₆] _{0.5}	0.095 ± 0.012
VI	[BMIM][BF ₄] _{0.75} [PF ₆] _{0.25}	0.100 ± 0.008
VI	[BMIM][BF ₄] _{0.9} [PF ₆] _{0.1}	0.157 ± 0.005

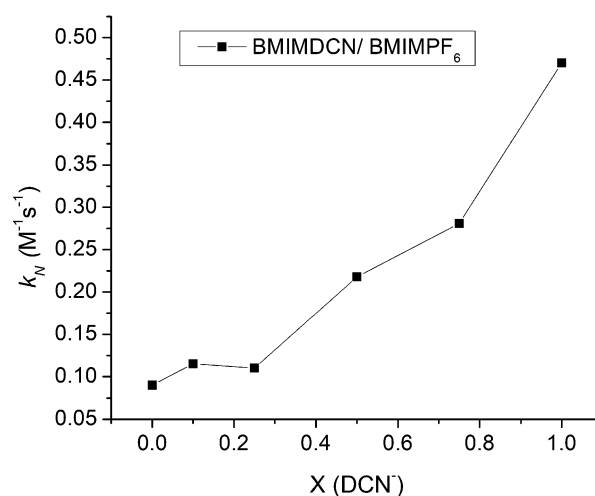


Fig. 2 Comparison between the rate constants and molar fraction in [BMIM][DCN]_a[PF₆]_b.

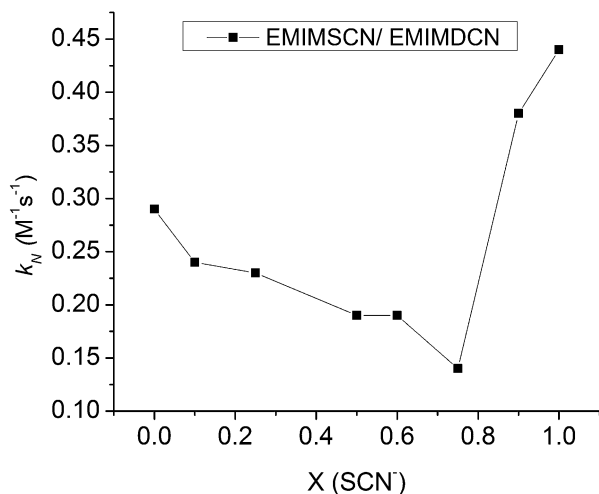


Fig. 3 Comparison between the rate constants and molar fraction in [EMIM][SCN]_a[DCN]_b.

The expected response is that by increasing the composition of [SCN⁻] there would be an increase in k_N ; a result traced to a greater number of molecules of thiocyanate ions in the first sphere of solvation. But in this case, as X_{SCN} increases, the values of the kinetic constant decrease until $X_{\text{SCN}} = 0.75$ and then increase when $X_{\text{SCN}} = 0.9$ (see Fig. 3). This result cannot be explained based on basicity only. Both ILs have similar basicities ($\beta_{\text{EMIMDCN}} = 0.63$ vs. $\beta_{\text{EMIMSCN}} = 0.57$). On the other hand, [SCN⁻] bears a negative charge on the sulphur atom that can delocalize towards the cyano group. On the other hand, [DCN⁻] has the negative charge on the nitrogen atom that can be delocalized towards two cyano substituents. Therefore, they can differ in the regional nucleophilicity of the central atom. Note that when $X_{\text{SCN}} < 0.75$ the anions compete for the key reaction site, thereby diminishing the k_N values. It may be concluded that in this regime, there is preferential solvation in favour of [DCN⁻]. It is also worth emphasizing that regardless of the composition of the mixtures within the zone $\{0.1 < X_{\text{SCN}} < 0.25\}$ and $\{0.5 < X_{\text{SCN}} < 0.6\}$, the kinetic response remains practically constant. This effect is known as the region of “iso-solvation”, which indicates that in a specific composition range of a mixture of solvents, the molecules considered (reactants, transition state, among others) are solvated by the same number of molecules of both solvents in the first solvation sphere (see Fig. 1).

(iv) In Family V, a response similar to that observed in families II and III is obtained, where increasing the X_{DCN} implies an increase in the kinetic constants. However, it is observed that within the region $\{0.25 < X_{\text{DCN}} < 0.75\}$, there is a larger range of composition where the iso-solvation effect is present. This phenomenon is better seen in Fig. 4. This kinetic response would be related to the fact that, despite a significant change in composition, the response in the rate coefficient is marginal.

Looking at Fig. 4, we may observe a significant region ranging from 0.2 to 0.75 in molar fraction of [DCN⁻], where the rate coefficient remains almost constant. We propose that this region may correspond to an iso-solvation zone, where the

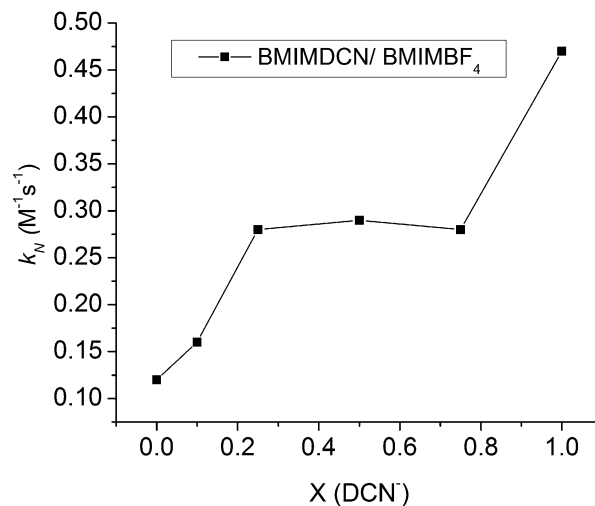


Fig. 4 Comparison between the rate constants and molar fraction in the [BMIM][DCN]_a[BF₄]_b mixture.

percentage of [DCN⁻] falls in a narrow range of about 60% in the first solvation shell. It is worth emphasising that this conclusion only holds if the reaction mechanism is the same for all the families studied.

(v) Finally, in Family VI, we can see an additional interesting phenomenon: for instance, for the point $X_{\text{BF}_4} = 0.9$ a marginally higher value of k_N is observed as compared to the pure IL (see Fig. 5). This point is in line with the hypothesis suggested by D'Anna *et al.*²³ who report that “mixing ILs differing in the size of the anions induces structural variation large enough to outweigh the effect of viscosity and consequently the kinetic outcome may be mainly dictated by the difference in structural organization induced by mixing”.

In order to find an explanation for the observed kinetic responses especially that related to a probable iso-solvation process, we performed an additional study of the basicity and polarity based on the Kamlet-Taft (KT) model.^{25–27} This model

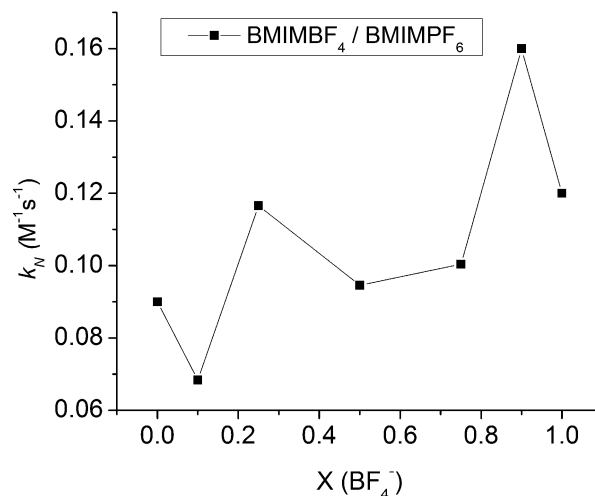


Fig. 5 Comparison between the rate constants and molar fraction in [BMIM][BF₄]_a[PF₆]_b.

Table 2 Kamlet and Taft parameters for the series of binary mixtures of ionic liquids considered in this study

Family	Mixture LI-LI in molar fractions	β	π^a
II	[BMIM][DCN] ₀ [PF ₆] ₁	0.30	1.03
II	[BMIM][DCN] _{0.1} [PF ₆] _{0.9}	0.37	1.04
II	[BMIM][DCN] _{0.5} [PF ₆] _{0.5}	0.55	1.08
II	[BMIM][DCN] _{0.9} [PF ₆] _{0.1}	0.72	1.13
II	[BMIM][DCN] ₁ [PF ₆] ₀	0.68	1.13
IV	[EMIM][SCN] ₀ [DCN] ₁	0.67	1.08
IV	[EMIM][SCN] _{0.2} [DCN] _{0.8}	0.77	1.18
IV	[EMIM][SCN] _{0.6} [DCN] _{0.4}	0.75	1.15
IV	[EMIM][SCN] _{0.75} [DCN] _{0.25}	0.91	1.30
IV	[EMIM][SCN] _{0.9} [DCN] _{0.1}	0.90	1.41
IV	[EMIM][SCN] ₁ [DCN] ₀	0.47	1.02
V	[BMIM][DCN] ₀ [BF ₄] ₁	0.37	1.02
V	[BMIM][DCN] _{0.1} [BF ₄] _{0.9}	0.43	1.09
V	[BMIM][DCN] _{0.5} [BF ₄] _{0.5}	0.46	1.15
V	[BMIM][DCN] _{0.9} [BF ₄] _{0.1}	0.61	1.18
V	[BMIM][DCN] ₁ [BF ₄] ₀	0.68	1.13
VI	[BMIM][BF ₄] ₀ [PF ₆] ₁	0.30	1.03
VI	[BMIM][BF ₄] _{0.1} [PF ₆] _{0.9}	0.37	1.04
VI	[BMIM][BF ₄] _{0.5} [PF ₆] _{0.5}	0.34	1.02
VI	[BMIM][BF ₄] _{0.9} [PF ₆] _{0.1}	0.27	1.04
VI	[BMIM][BF ₄] ₁ [PF ₆] ₀	0.37	1.02

^a The parameter α cannot be determined in mixtures using the KT protocol.

describes solvation effects in terms of a multiparametric relationship including the parameter α , representing the acidity of the solvent, which is related to the ability of donating a hydrogen bond (HB) to the substrate; the parameter β , measuring the basicity of the solvent or its ability to receive a HB from the substrate, and finally the parameter π^* accounting for the polarity of the solvent. Since we are mainly dealing with the “anion” effect, we restrict the study to the β and π^* parameters. Furthermore, the parameter α could not be measured in this study because the values obtained for IL mixtures are outside the allowed range for this model.^{35,36} The results are summarized in Table 2.

For the mixture [BMIM][DCN]_a[PF₆]_b and [BMIM][DCN]_a[BF₄]_b the comparisons between the rate coefficient and the basicity parameter β are in general quite similar to that discussed on the basis of the k_N values and composition. For instance, with respect to the β parameter, as X_{DCN} increases, the basicity of the mixture increases (see Fig. 6A and B respectively).

Note that for the EMIM series, similar iso-solvation patterns can be observed (see the ESI,† Fig. S17 and S18).

With respect to the solvent polarity parameter π^* the variation is not significant (see Fig. 7). This result is not surprising because for pure ionic liquids, it has been reported that their polarity, mainly given by their dielectric constants,³⁷ fall within a narrow range of variations. For mixtures of ILs a similar response is not surprising.

Experimental

Kinetic measurements

Kinetic measurements were carried out spectrophotometrically (330–500 nm range) by means of a diode array spectrophotometer

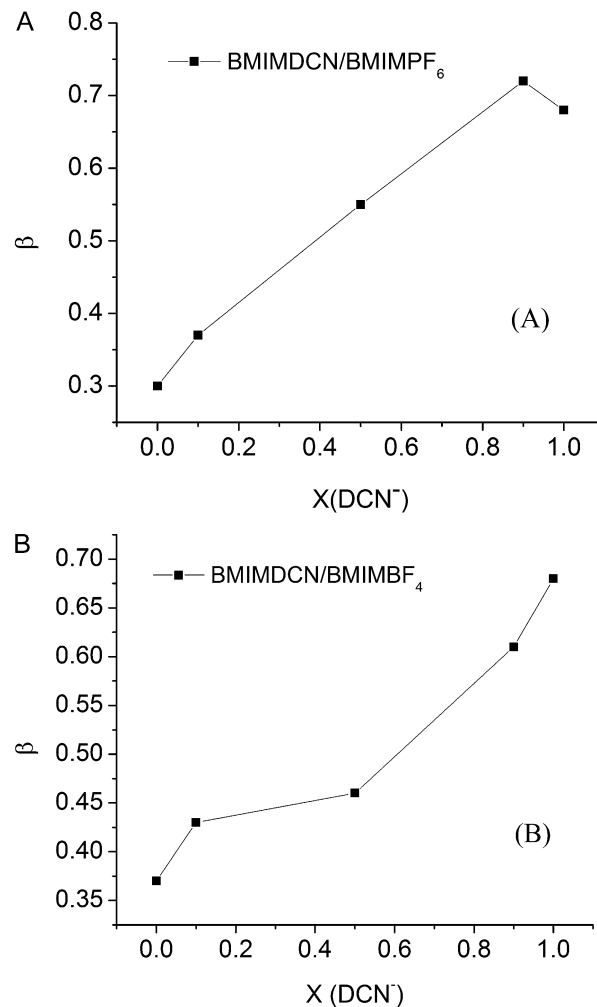


Fig. 6 (A) Comparison between β parameters and the molar fraction in [BMIM][DCN]_a[PF₆]_b. (B) Comparison between β parameters and the molar fraction in [BMIM][DCN]_a[BF₄]_b.

in mixtures of ionic liquids at 25 ± 0.1 °C. The reactions, studied under excess of amine over the substrate, were started by injection of a substrate stock solution in acetonitrile into the amine solution in the IL-IL mixture (1000 μL in the spectrophotometric cell). Under these conditions, pseudo first order rate coefficients (k_{obs}) were found. Rate coefficient values for morpholine (k_N) were obtained from plots of k_{obs} vs. [amine]. The experimental k_{obs} values are listed in Tables S1–S14 and Fig. S15–S18 in the ESI.†

Product study

The presence of 4-(2,4-dinitrophenyl) morpholine as a product of the reactions was determined spectrophotometrically by comparison of the UV-visible spectra obtained at the end of the reactions with those of authentic samples obtained under the same conditions.

Determination of Kamlet–Taft parameters

The solvent parameters were measured by injecting the binary mixtures of ILs (950 μL) into a quartz cuvette of optical path 1.0 cm with the probes (Reichardt Dye, 4-nitroaniline, and

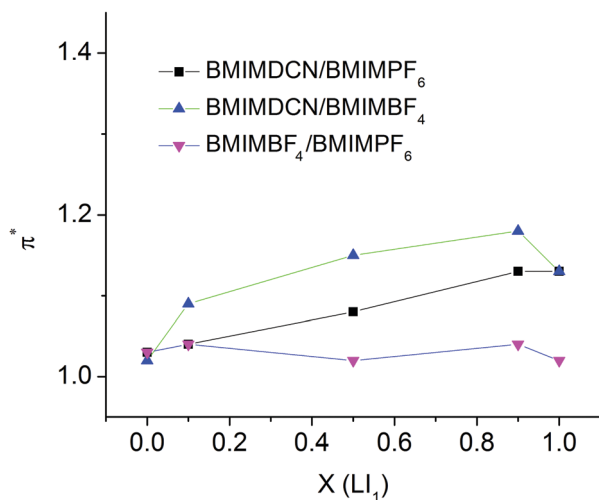


Fig. 7 Comparison between the π^* parameter and the molar fraction in [BMIM][DCN]_a[PF₆]_b, [BMIM][DCN]_a[BF₄]_b and [BMIM][BF₄]_a[PF₆]_b.

N,N-diethyl-4-nitroaniline) previously prepared in acetone (50 μ L of stock solution of the probes was evaporated to dryness for 30 minutes). The concentration of the stock solution was 1.85×10^{-3} M. All the solutions were thermostated at 25 ± 0.1 °C.

Purity of the ionic liquids

The series of ionic liquids used were purchased from Merck, and used as delivered. The specifications are as follows: purity (HPLC) > 98%; identity (NMR) passed test; halides (IC) < 0.1%; water (KF) < 0.1%.

Conclusions

A systematic kinetic study on the S_NAr reaction in a series of mixtures of ionic liquids has been presented. This reaction has been selected as a model system because its kinetics in pure ILs is well documented in the literature. The main outcomes of the present study are the following:

Iso-solvation regimes were observed for 4 mixtures including [EMIM][SCN][DCN], [BMIM][DCN][BF₄], [BMIM][BF₄][PF₆] and [BMIM][PF₆][FAP]. The results show that for significant changes in composition, the rate coefficients remain approximately constant. An additional interesting result is that for the mixture [BMIM][BF₄][PF₆] (in the proportion of 0.9 for the molar fraction of BMIMBF₄), a slightly better kinetic response is observed, as compared to pure BMIMBF₄ and BMIMPF₆. Finally, for the [EMIM][SCN][DCN] mixture, an increasing proportion of EMIMSCN with respect to EMIMDCN results in a decrease of the rate coefficient within the range {0.1–0.75} for the molar fraction of EMIMSCN. This result may be traced to competition between the anions [SCN⁻] and [DCN⁻] towards the reaction centre driven by the basicity of the reaction medium.

Conflicts of interest

There are no conflicts to declare.

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