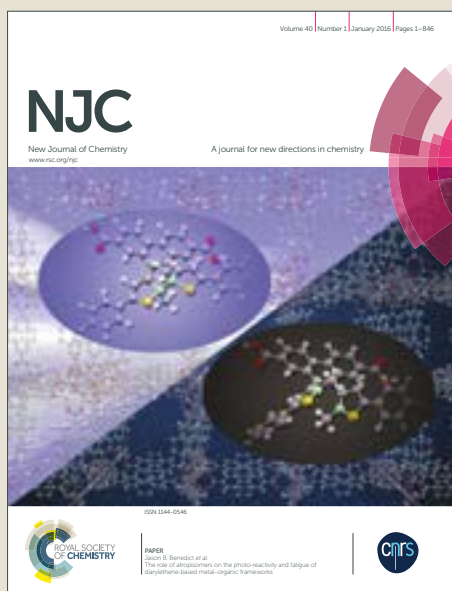


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Iso-Solvation Effects in Mixtures of Ionic Liquids on the Kinetics of a model S_NAr Reaction

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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) is 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 remains approximately constant. An additional interesting result is that for the mixture [BMIM][BF₄][PF₆] (in the proportion 0.9 in molar fraction of BMIMBF₄), the mixture shows a slightly better kinetic performance as compared to the pure BMIMBF₄ and BMIMPF₆. Finally, for the [EMIM][SCN][DCN] mixture, an increasing proportion of EMIMSCN respect to EMIMDCN result in a decrease of the rate coefficient within the range {0.1 - 0.75} in molar fraction of EMIMSCN. This result may be traced to a competition between the anions [SCN] and [DCN] towards the reaction center driven by the basicity of the reaction medium.

Introduction

The use of solvent conventional mixtures has largely been documented in literature.¹⁻⁵ These studies have been extended to mixtures involving conventional solvent/ionic liquids⁶⁻¹⁰ and mixtures of ionic liquids.¹¹⁻¹⁴ Apart of the solvating properties of these systems, most of them 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 (HB), density, melting point, 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 (IL) is that the problem implies a three-body problem. Remember that, IL are generally associated to a very low extent¹⁸ and therefore one has to lead with interactions between the substrate with a non-associated cation/anion pair.¹⁹ Note also, that in the case of IL, 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 IL was fixed, since there are antecedents for the reaction under study,

pointing out to a 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 IL 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 IL respect to their mixtures, thereby attributing this response to the ability of [OAc⁻] to form complexes with the [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 from our group, regarding the importance of the size, polarizability and ability to form HB of the anion (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 result mainly responds 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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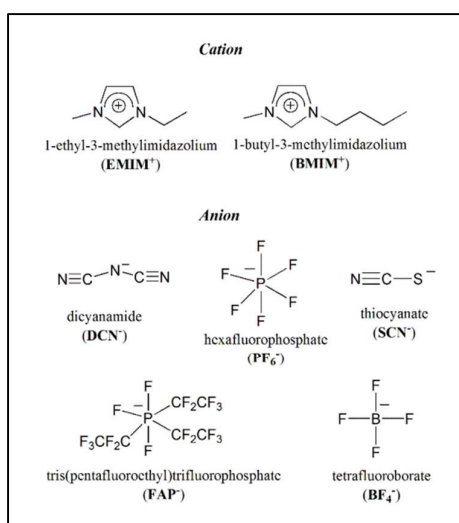
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Kirchner et al.²⁴ performed a combined theoretical-experimental study, based on molecular dynamics, to simulate the environment in mixtures of IL respect to pure IL. Complementing with NMR study, they investigated changes in chemical shifts of hydrogen 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 property 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 model²⁵⁻²⁷ 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 IL were selected from a series of IL used in a previous work²⁰ in which the same reaction was studied in pure IL (see Scheme I), with the aim of analysing any additional information that could be present with reference to the mixture. Scheme I summarize the series of IL 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 in pure IL. It should be emphasized that the analysis of 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 respect to the pure solvents.³²



Scheme I. Cation / anion structures used in this study.

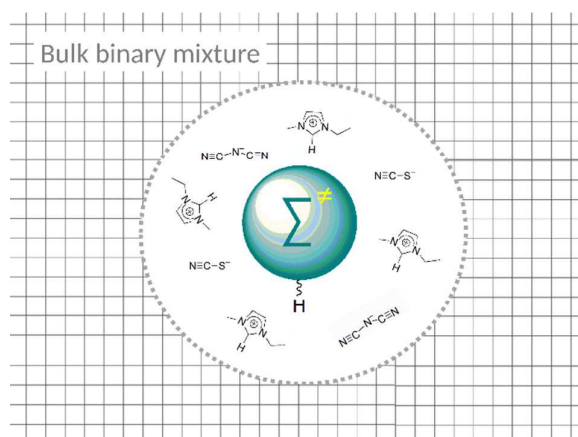
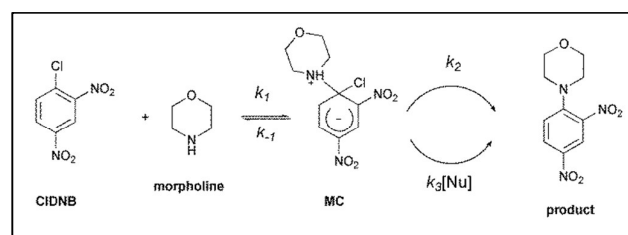


Figure 1. Schematic representation of iso-solvation for a hypothetical mixture of [EMIM]/[SCN][DCN]. The scheme represents "the first" sphere of solvation in the mixture, where the probe Σ represents the activated substrate.

The concept of iso-solvation has been introduced to indicate the composition of a mixture in which the probe under 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 Figure 1.

Results and discussion

The studied reaction follows an aromatic nucleophilic substitution (S_NAr) pathway in experimental conditions of pseudo first order. The S_NAr is a stepwise mechanism, where the first step leads to the formation of a zwitterionic complex named Meisenheimer Complex (MC) from which two process 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 loss the LG to give the reaction product.^{33,34} In the experimental conditions used only one kinetic product was spectrophotometrically observed for all the reaction studied. See Scheme II.



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

The kinetic analysis shows that the pseudo first order rate constant (k_{obs}) for all the study can be expressed as Eq. 1, in which [Nu] represents the concentration of 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 plotted through of k_{obs} vs. [Nu] in order to obtain the nucleophilic attack rate constants (k_N) values from Eq. 2.

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

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

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

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 hydrogen bond; *ii*) significant differences in kinetic constant (k_N) relative to pure IL; *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 in the cation imidazolium (EMIM⁺ and BMIM⁺) with different anions (see Scheme I). 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.

Table 1. Rate constants 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

Table 1. (Continued).

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

The most important observations after inspection of Table 1 are as follows: *i*) in Family I, if we compare both IL separately (i.e. pure IL), k_N values in BMIMPF₆ are higher than in BMIMFAP; both anions presenting similar coordination number (see Scheme I), 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} in [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 pure IL ($\beta_{BMIMPF_6} = 0.30$ vs. $\beta_{BMIMFAP} = 0.15$).

ii) If we now separate Family I and compare it with respect to the IL that has the highest rate constant (BMIMDCN) as reference, we obtain Families II and III. We can see that the effects of anion size predominate again because [DCN⁻] is smaller than [PF₆⁻] and [FAP⁻] and more basic than both ($\beta_{BMIMDCN} = 0.68$) (see Figure S16 in 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 Figure 2).

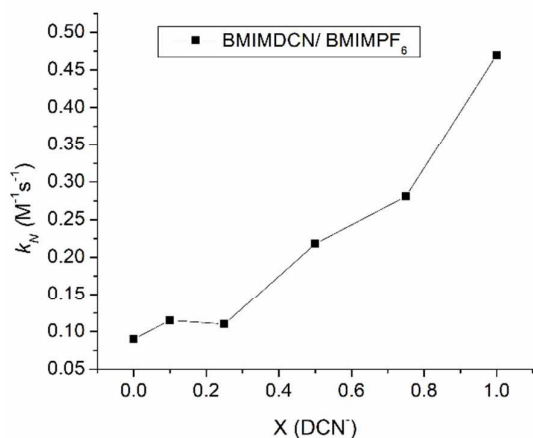


Figure 2. Comparison between the rate constants and molar fraction in $[BMIM][DCN]_a[PF_6]_b$.

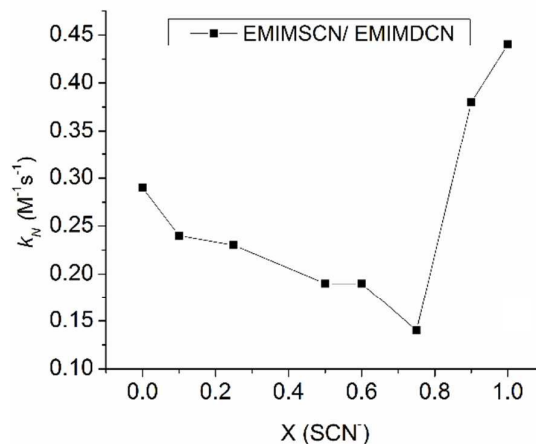


Figure 3. Comparison between the rate constants and molar fraction in $[EMIM][SCN]_a[DCN]_b$.

iii) For Family IV, the cation change to $[EMIM^+]$ this time. Both IL 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. 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 ion in the first sphere of solvation. But in this case, as X_{SCN} increases, the values of the kinetic constant decrease until $X_{SCN} = 0.75$ and then increases when $X_{SCN} = 0.9$ (see Figure 3). This result cannot be explained based on basicity only. Both IL have similar basicities, ($\beta_{EMIMDCN} = 0.63$ vs. $\beta_{EMIMSCN} = 0.57$). 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 $X_{SCN} < 0.75$ 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 $\{0.1 < X_{SCN} < 0.25\}$ and $\{0.5 < X_{SCN} < 0.6\}$, 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 solvent in the first solvation sphere (see Figure 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 $\{0.25 < X_{DCN} < 0.75\}$, there is a larger range in composition where the iso-solvation effect is present. This phenomenon is better seen in Figure 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 Figure 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 percentage of $[DCN^-]$ falls in a narrow range of about 60% in the first solvation shell. It is worth emphasizing that this conclusion only holds if the reaction mechanism is the same for all the families studied.

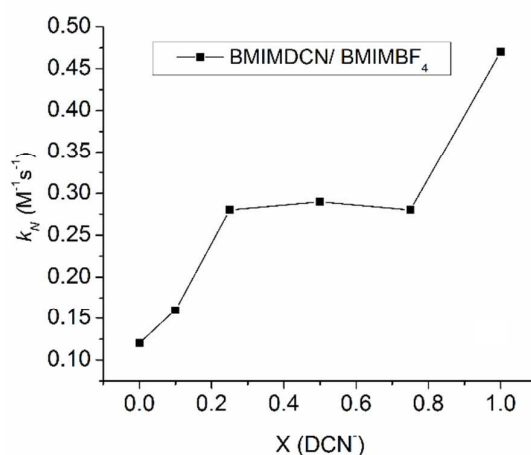


Figure 4. Comparison between the rate constants and molar fraction in $[BMIM][DCN]_a[BF_4]_b$ mixture.

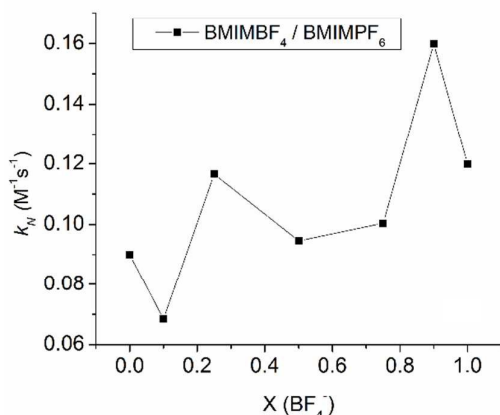


Figure 5. Comparison between the rate constants and molar fraction in $[\text{BMIM}][\text{BF}_4]_a[\text{PF}_6]_b$.

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 pure IL. (see Figure 5). This point is in line with the hypothesis suggested by D'Anna et al.²³ who report that "mixing IL differing for 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 Kamlet-Taft (KT) model.²⁵⁻²⁷ This model 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.

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^*
II	$[\text{BMIM}][\text{DCN}]_0[\text{PF}_6]_1$	0.30	1.03
II	$[\text{BMIM}][\text{DCN}]_{0.1}[\text{PF}_6]_{0.9}$	0.37	1.04
II	$[\text{BMIM}][\text{DCN}]_{0.5}[\text{PF}_6]_{0.5}$	0.55	1.08
II	$[\text{BMIM}][\text{DCN}]_{0.9}[\text{PF}_6]_{0.1}$	0.72	1.13
II	$[\text{BMIM}][\text{DCN}]_1[\text{PF}_6]_0$	0.68	1.13

Table 2. (Continued).

Family	Mixture LI-LI In molar fractions	β	π^*
IV	$[\text{EMIM}][\text{SCN}]_0[\text{DCN}]_1$	0.67	1.08
IV	$[\text{EMIM}][\text{SCN}]_{0.2}[\text{DCN}]_{0.8}$	0.77	1.18
IV	$[\text{EMIM}][\text{SCN}]_{0.6}[\text{DCN}]_{0.4}$	0.75	1.15
IV	$[\text{EMIM}][\text{SCN}]_{0.75}[\text{DCN}]_{0.25}$	0.91	1.30
IV	$[\text{EMIM}][\text{SCN}]_{0.9}[\text{DCN}]_{0.1}$	0.90	1.41
IV	$[\text{EMIM}][\text{SCN}]_1[\text{DCN}]_0$	0.47	1.02
V	$[\text{BMIM}][\text{DCN}]_0[\text{BF}_4]_1$	0.37	1.02
V	$[\text{BMIM}][\text{DCN}]_{0.1}[\text{BF}_4]_{0.9}$	0.43	1.09
V	$[\text{BMIM}][\text{DCN}]_{0.5}[\text{BF}_4]_{0.5}$	0.46	1.15
V	$[\text{BMIM}][\text{DCN}]_{0.9}[\text{BF}_4]_{0.1}$	0.61	1.18
V	$[\text{BMIM}][\text{DCN}]_1[\text{BF}_4]_0$	0.68	1.13
VI	$[\text{BMIM}][\text{BF}_4]_0[\text{PF}_6]_1$	0.30	1.03
VI	$[\text{BMIM}][\text{BF}_4]_{0.1}[\text{PF}_6]_{0.9}$	0.37	1.04
VI	$[\text{BMIM}][\text{BF}_4]_{0.5}[\text{PF}_6]_{0.5}$	0.34	1.02
VI	$[\text{BMIM}][\text{BF}_4]_{0.9}[\text{PF}_6]_{0.1}$	0.27	1.04
VI	$[\text{BMIM}][\text{BF}_4]_1[\text{PF}_6]_0$	0.37	1.02

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

For the mixture $[\text{BMIM}][\text{DCN}]_a[\text{PF}_6]_b$ and $[\text{BMIM}][\text{DCN}]_a[\text{BF}_4]_b$, 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 the X_{DCN} increases, the basicity of the mixture increases (see Figure 6A and 6B respectively).

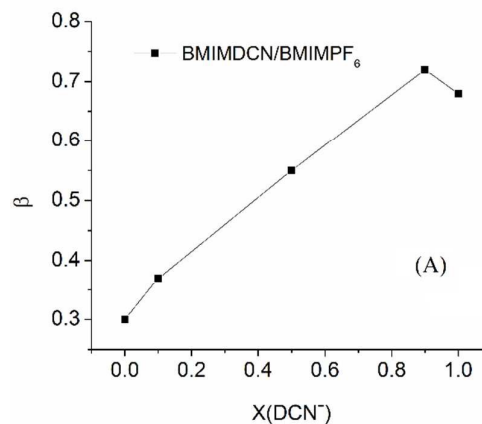


Figure 6A. Comparison between β parameters and molar fraction in $[\text{BMIM}][\text{DCN}]_a[\text{PF}_6]_b$.

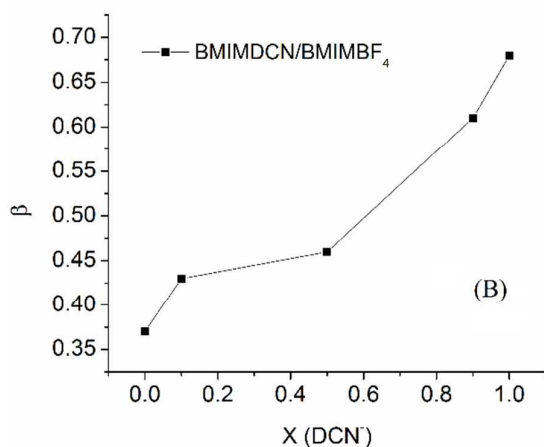


Figure 6B. Comparison between β parameters and molar fraction in $[\text{BMIM}][\text{DCN}]_a[\text{BF}_4]_b$.

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

With respect to the solvent polarity parameter π^* the variation is not significant (see Figure 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 IL a similar response is not surprising.

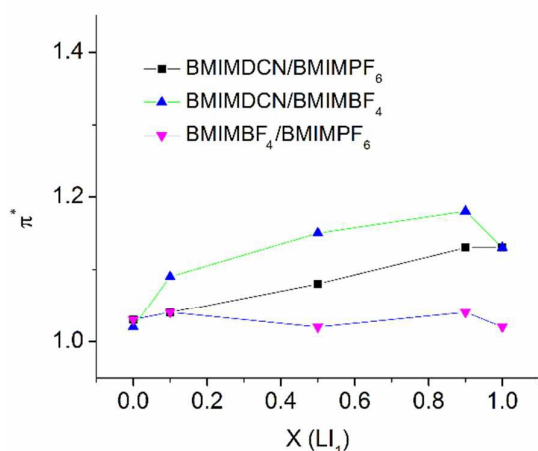


Figure 7. Comparison between π^* parameter and molar fraction in $[\text{BMIM}][\text{DCN}]_a[\text{PF}_6]_b$, $[\text{BMIM}][\text{DCN}]_a[\text{BF}_4]_b$ and $[\text{BMIM}][\text{BF}_4]_a[\text{PF}_6]_b$.

Experimental

Kinetic Measurements

Kinetic measurement was carried out spectrophotometrically (330-500 nm range) by means of a diode array spectrophotometer in mixtures of ionic liquids at 25 ± 0.1 °C. The reactions, studied under excess of the amine over the substrate, were started by injection of a substrate stock solution in acetonitrile into the amine solution in 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 Figures S15-S18 in the Electronic Supporting Information.

Product study

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

Determination of Kamlet-Taft parameters

The solvent parameters was measured by injecting the binary mixtures of IL (950 μL) into a quartz cuvette of optical path 1.0 cm with the probes (Reichardt Dye, 4-nitroaniline, and N,N-diethyl-4-nitroaniline) previously prepared in acetone (50 μL 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 $\text{S}_{\text{N}}\text{Ar}$ reaction in a series of mixtures of ionic liquids has been presented. This reaction has been selected as model system because its kinetic in pure IL is well documented in literature. The main outcomes of the present study are the following:

Iso-solvation regimes were observed for 4 mixtures including $[\text{EMIM}][\text{SCN}][\text{DCN}]$, $[\text{BMIM}][\text{DCN}][\text{BF}_4]$, $[\text{BMIM}][\text{BF}_4][\text{PF}_6]$ and $[\text{BMIM}][\text{PF}_6][\text{FAP}]$. The results show that for significant changes in composition, the rate coefficients remain approximately constant. An additional interesting result is that for the mixture $[\text{BMIM}][\text{BF}_4][\text{PF}_6]$ (in the proportion 0.9 in molar fraction of BMIMBF_4), a slightly better kinetic response is observed, as compared to the pure BMIMBF_4 and BMIMPF_6 . Finally, for the $[\text{EMIM}][\text{SCN}][\text{DCN}]$ mixture, an increasing proportion of EMIMSCN respect to EMIMDCN result in a decrease of the rate coefficient within the range {0.1 - 0.75} in

molar fraction of EMIMSCN. This result may be traced to a competition between the anions [SCN⁻] and [DCN⁻] towards the reaction centre driven by the basicity of the reaction medium.

Conflicts of interest

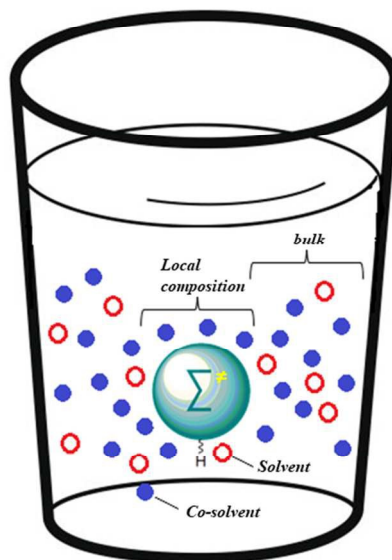
There are no conflicts to declare.

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