

Ionic Liquid Solvent Effects

Gutmann's Donor Numbers Correctly Assess the Effect of the Solvent on the Kinetics of S_NAr Reactions in Ionic Liquids

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Abstract: We report an experimental study on the effect of solvents on the model S_NAr reaction between 1-chloro-2,4-dinitrobenzene and morpholine in a series of pure ionic liquids (IL). A significant catalytic effect is observed with reference to the same reaction run in water, acetonitrile, and other conventional solvents. The series of IL considered include the anions, NTf_2^- , DCN^- , SCN^- , $CF_3SO_3^-$, PF_6^- , and FAP^- with the series of cations 1-butyl-3-methylimidazolium ($[BMIM]^+$), 1-ethyl-3-methylimidazolium ($[EMIM]^+$), 1-butyl-2,3-dimethylimidazolium ($[BM_2IM]^+$), and 1-butyl-1-methyl-

pyrrolidinium ($[BMPyr]^+$). The observed solvent effects can be attributed to an "anion effect". The anion effect appears related to the anion size (polarizability) and their hydrogen-bonding (HB) abilities to the substrate. These results have been confirmed by performing a comparison of the rate constants with Gutmann's donicity numbers (DNs). The good correlation between rate constants and DN emphasizes the major role of charge transfer from the anion to the substrate.

Introduction

Nucleophilic aromatic substitution (S_NAr) reactions have been studied in conventional organic solvents (COS)^[1–6] and more recently in ionic liquids (ILs).^[7–11] For instance, Welton et al.^[7] reported the design of task-specific ILs by using theoretical methods to optimize those IL properties that are best suited for the S_NAr processes. The descriptor proposed by these authors is the deprotonation Gibbs free energy of the conjugated acid of the anion, which is expected to be highly correlated with the hydrogen-bond (HB) basicity of the IL. They reported a dramatic increase in yield above that possible to achieve in the best molecular solvent. Harper et al., on the other hand, reported the importance of the IL structure on the reaction rate of S_NAr processes in pure ILs and mixtures of ILs and COS.^[12] These authors concluded that the microscopic origins of the observed second-order rate enhancements are strongly IL dependent. These reports prompted us to perform a systematic study on the electronic structure origin of solvent effects pro-

moted by IL media on S_NAr reactions. The main focus of this work is on the evaluation of two models of solvent effects, which incorporate the HB abilities of the cations and anions forming the IL, and implicitly rely on the Lewis acidity/basicity parameters for a series of ILs. The first model is the well-known Kamlet–Taft equation,^[13–15] which has been used to study solvent effects in ILs for several organic reactions.^[16–25] The second model, less used, considers Gutmann's donor and acceptor numbers,^[26,27] which can be deduced from calorimetric measurements or from NMR chemical shifts of ^{23}Na and ^{31}P .^[28] The evaluation of both scales of solvent effects in ILs is compared with the rate coefficients for the S_NAr reaction of 1-chloro-2,4-dinitrobenzene and morpholine. Scheme 1 includes the structure and acronyms of the ILs used in this work (15 ILs total).

Results and Discussion

Table 1 shows the kinetic data recorded for the model S_NAr reaction carried out in the series of 15 IL reported herein.

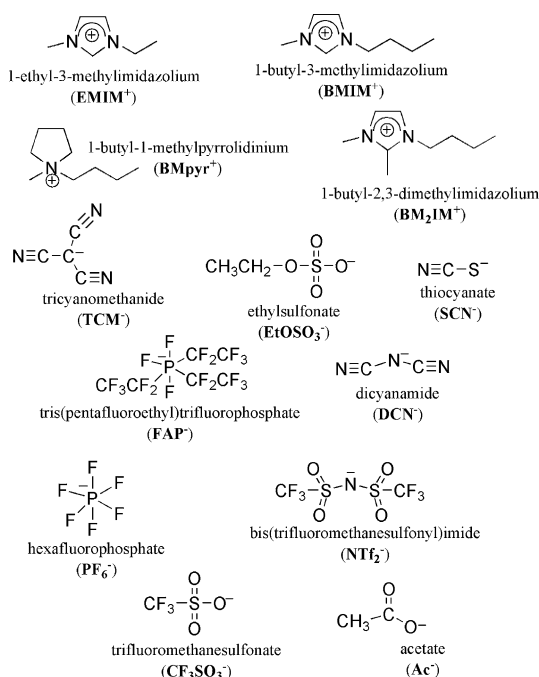
Table 1 shows the observed rate coefficients for the title reaction in three series of IL, namely, $[BMIM]^+$, $[EMIM]^+$, and $[BMPyr]^+$ based ILs with varying counter ions. One IL based on $[BM_2IM]^+$ was considered to study the effect of blocking the acidic hydrogen atom attached to the C_2 site of the imidazolium cation (see Scheme 1). The best solvent within the whole series of IL studied is $[BMIM]DCN$. Within this series, it becomes clear that the rate coefficients appear to be clearly correlated with the accompanying anion. If we consider that both DCN^- and SCN^- are the smallest anions within the series, it may first be concluded that anion size is relevant for the observed kinetic response. Note that the rate constant for nucleophilic attack,

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Scheme 1. Chemical structures for the series of cations and anions of the ionic liquids used in this study.

Table 1. Rate coefficient values for the reaction of morpholine with 1-chloro-2,4-dinitrobenzene in ionic liquids at 25 ± 0.1 °C.

Ionic liquid	k_N [$M^{-1} s^{-1}$]	Ionic liquid	k_N [$M^{-1} s^{-1}$]
[BMIM]DCN	0.47 ± 0.01	[EMIM]DCN	0.29 ± 0.01
[BMIM]SCN	0.32 ± 0.01	[EMIM]SCN	0.44 ± 0.02
[BMIM]CF ₃ SO ₃	0.30 ± 0.01	[EMIM]CF ₃ SO ₃	0.15 ± 10^{-3}
[BMIM]PF ₆	0.09 ± 10^{-3}	[EMIM]NTf ₂	0.07 ± 10^{-3}
[BMIM]NTf ₂	0.07 ± 0.01	[EMIM]FAP	0.02 ± 10^{-3}
[BMIM]FAP	0.02 ± 10^{-4}	[BMPyr]DCN	0.25 ± 0.01
BM ₂ IMNTf ₂	0.08 ± 10^{-3}	[BMPyr]CF ₃ SO ₃	0.14 ± 0.01
		[BMPyr]NTf ₂	0.06 ± 10^{-3}

k_N is about 23.5 times faster for [BMIM]DCN compared with [BMIM]FAP, the IL containing the biggest anion of the series. Note also that the comparison between [BMIM]DCN with [BMIM]SCN gives only an improvement factor of 1.5 in favor of DCN⁻. This result suggests that, apart from anion size, there is an additional effect that can be attributed to the electronic polarizability: DCN⁻ is expected to be significantly more polarizable than SCN⁻ owing to the presence of a π -electron-rich zone. Note finally that the comparison between [BMIM]NTf₂ and [BM₂IM]NTf₂ emphasizes the observed anion effect within this series: the effect of blocking the acidic hydrogen atom at C₂ results in almost identically kinetic responses. This result suggests that the probable “cation solvent effect” is marginal.

Within the [EMIM]⁺ series, some similar trends are maintained with respect to the [BMIM]⁺ series. Here, the main change is the shortening of the alkyl chain at the cation, which results in an inversion in the values of the rate coefficient in favor of SCN⁻ this time. Finally, within the series of [BMPyr]⁺,

we again found a size + polarizability anion effect. In summary, the change from [BMIM]⁺ to [EMIM]⁺ reveals that the best IL media are those bearing small and highly polarizable anions, independent of the cation present in the IL: compare, for instance, $k_N = 0.47 M^{-1} s^{-1}$ and $0.44 M^{-1} s^{-1}$ for [BMIM]DCN and [EMIM]SCN, respectively.

On the other hand, previous studies have shown that [BMIM]DCN is a highly basic IL that in some reactions can present catalytic properties, thereby qualifying it as a task-specific solvent for S_NAr reactions.^[29] Therefore, the possibility of establishing an advanced bond between the hydrogen atom of the amine moiety of morpholine and the nitrogen atom of dicyanamide is highly expected. As a result, the nucleophilicity of the nitrogen atom in morpholine is enhanced. Note further that the rate coefficient values in [BMIM]DCN with respect to [EMIM]DCN or [BMPyr]DCN is increased by approximately two times. On the other hand, [EMIM]⁺ cations present significant differences in electron delocalization patterns and number of nitrogen atoms compared with [BMPyr]⁺ cations, yet the rate coefficients are similar. In other words, the reactivity observed in this system suggests that the “anion effect” outweighs the “cation solvent effect”. These results confirm the hypothesis proposed by Harper et al. in the sense that the structure of the IL may become a determinant factor affecting the S_NAr reactivity.^[12]

To interpret the solvation effects on the recorded kinetic responses of the title reaction, we performed two different analysis based on solvatochromic and NMR chemical shift measurements. The first one, is one of the preferred models to analyze solvent effects in ILs.^[16–25] It is based on a multivariate empirical equation that includes the following parameters: hydrogen bond acidity (α), measuring the ability of the IL to donate a HB to the substrate; hydrogen bond basicity (β), measuring the ability of the IL to accept a HB from the substrate; and a parameter π^* , measuring the dipolar polarizability of the IL. Prior to applying this technique to analyze the effect of the solvent on the kinetic responses observed for the model S_NAr reaction, we shall comment on the limitations that this model presents. The main drawback was nicely explained by Welton et al.,^[30] who emphasized that, in general, Kamlet–Taft (KT) parameters miss the main ion–ion interactions expected for any substrate dissolved in an IL at ambient conditions, because the probes used to temperate the KT parameters are at most zwitterionic, not ionic. This result is relevant as it affects the completeness of the model severely because the best ILs are those that are associated to a very low extent. In this sense, independent of the technical quality of the KT parameters, all of them bear a *caveat emptor* warning for all the potential users of these scales. The second weakness of the KT technique is related to the interpretation of the α and β parameters. Whereas α is associated with the HB acidity of the IL, and therefore associated with the cation forming the IL, the β parameter is always associated with the anion component of the IL. This simplistic assignation has been recently put into jeopardy, because in [BMIM]⁺ based ILs, both the HB acidity and HB basicity may be located at the cation, an effect that is, however, anion-dependent through polarization effects.^[31]

Table 2. Kamlet–Taft parameters for the ionic liquids considered in this work.

Ionic liquid	α	β	π^*
[BMIM]DCN	0.51 ^[a]	0.68 ^[a]	1.13 ^[a]
[BMIM]SCN	— ^[c]	0.57 ^[a]	1.08 ^[a]
[BMIM]CF ₃ SO ₃	0.62 ^[a]	0.44 ^[a]	1.04 ^[a]
[BMIM]PF ₆	0.63 ^{[b][c]}	0.30 ^[a]	1.03 ^[b]
[BMIM]NTf ₂	0.72 ^{[b][c]}	0.24 ^[b]	0.90 ^[b]
[BMIM]FAP	0.65 ^[a]	0.15 ^[a]	0.89 ^[a]
[EMIM]DCN	0.53 ^[a]	0.63 ^[a]	1.11 ^[a]
[EMIM]SCN	— ^[c]	0.57 ^[a]	1.04 ^[a]
[EMIM]CF ₃ SO ₃	— ^[c]	0.40 ^[a]	1.18 ^[a]
[EMIM]NTf ₂	0.71 ^{[b][c]}	0.29 ^[a]	0.93 ^[a]
[EMIM]FAP	0.58 ^[a]	0.11 ^[a]	1.04 ^[a]
[BM ₂ IM]NTf ₂	0.38 ^[b]	0.26 ^[b]	1.02 ^[b]
[BMPyr]DCN	0.29 ^[a]	0.52 ^[a]	1.18 ^[a]
[BMPyr]CF ₃ SO ₃	— ^[c]	0.59 ^[a]	0.89 ^[a]
[BMPyr]NTf ₂	0.43 ^{[b][c]}	0.34 ^[a]	1.02 ^[a]

[a] This work. [b] From reference [32]. [c] The parameter could not be determined because the Reichardt probe reacts with the corresponding IL.

Table 2 shows the Kamlet–Taft parameters for the series of ILs considered in this work.

With this set of data at hand, we attempted to perform a multivariate regression procedure of the form shown in Equation (1), a procedure that systematically failed.

$$\log k_N = a_0 + a_1\alpha + a_2\beta + a_3\pi^* \quad (1)$$

The statistical test suggested a poor correlation, which was attributed to the linear dependence among the set of α , β , and π^* variables, and also as a result of the low number of the samples. The linear (or non-linear) dependence among the acidity and basicity parameters is not surprising because the product of their corresponding activities are equal to a constant. On the other hand, the polarizability parameter π^* may be related to the softness or hardness of the components of the IL, a concept that is also related to charge transfer. The only possibility of relating the kinetic data condensed in the rate coefficient k_N and the set of parameters α , β , and π^* is to perform the comparisons separately. However, during the first revision of this manuscript, one of the reviewers persuasively convinced us that plotting rates against single orthogonal variables in KT analysis is completely inappropriate.

To settle the origin of the solvent effect of the ILs on the model S_NAr reaction, we considered a second alternative model based on the donor (DN) and acceptor (AN) numbers proposed by Viktor Gutmann,^[26,27] which have been recently re-formulated to describe acid/base solvent properties in ILs by Schmeisser et al.^[28] According to the original definition proposed by Gutmann, DN and AN descriptors are a quantitative measure of Lewis basicity and acidity of a solvent (generally a non-aqueous one), respectively. These numbers can be measured by using two different techniques, namely, calorimetrically or by using the chemical shift in ³¹P NMR spectra. These parameters are widely used in inorganic chemistry to describe the ability of solvents to donate or accept electron pairs or at

least electron density to the substrate. Gutmann defined the DN as the positive ΔH value of the reaction of a donor solvent with the acceptor halide antimony(V) chloride in an inert medium, such as 1,2-dichloroethane, and this parameter represents a measure for the donor properties of a solvent. On the other hand, ANs are derived from ³¹P NMR measurements of tri-ethyl-phosphine oxide dissolved in the respective solvents. The AN is a measure of the electrophilic properties of a solvent. Recently, the DN has been evaluated for ILs with a different technique, that is, by using ²³Na NMR spectroscopy, which describes with good results the ability of the solvent to donate electron density to a reference compound. The authors proposed that, whereas DNs show a strong dependence on the anionic component of the ionic liquids, the AN is dependent on both the anionic and cationic components of the IL.^[28] These results are suitable for our purposes because, if we consider the kinetic data, these point to the solvent effect of the ILs on the S_NAr reactions being mostly anion dependent. These results also strongly agree with those previously reported by Welton et al.^[7] Thus, the correlation between k_N values and DN is expected to be significant. To prove this hypothesis, we compared the k_N values with the set of DN available for the [EMIM]⁺ series, as shown in Table 3.

Table 3. Donor and acceptor numbers and experimental k_N values for the [EMIM]⁺ series.^[a]

Ionic liquid	Donor number [kcal mol ⁻¹]	Acceptor number [kcal mol ⁻¹]	k_N [M ⁻¹ s ⁻¹]
[EMIM]FAP	−12.3	29.3	0.02
[EMIM]NTf ₂	11.2	27.4	0.07
[EMIM]CF ₃ SO ₃	20.4	37.1	0.15
[EMIM]DCN	37.8	31.7	0.29
[EMIM]SCN	45.9	32.4	0.44
[EMIM]Ac	43.3	29.4	0.41 ^[b]
[EMIM]TCM	26.1	—	0.16 ^[b]
[EMIM]EtOSO ₃	22.3	25.0	0.13 ^[b]

[a] The structures of the new ILs are in Scheme 1. [b] Values of k_N predicted from Equation (2).

The result of such a comparison is depicted in Figure 1. It may be seen that this time the comparison is almost quantitative. The resulting empirical equation is:

$$\log k_N = 0.02 \text{ DN} - 1.39 \quad (2)$$

This empirical equation is useful as it permits the prediction of the k_N value from the corresponding DN. For instance, the DN value for [EMIM]Ac (DN = 43.3 kcal mol⁻¹) predicts that the k_N value should be expected around 0.41 M⁻¹ s⁻¹. This prediction awaits experimental verification. However, this figure makes sense according to the empirical rule deduced from Table 1: the best IL is that bearing a small and polarizable anion. For [EMIM]TCM (DN = 26.1 kcal mol⁻¹), the predicted k_N value should be around 0.16 M⁻¹ s⁻¹, which is also a coherent prediction because, according to the kinetic data recorded in

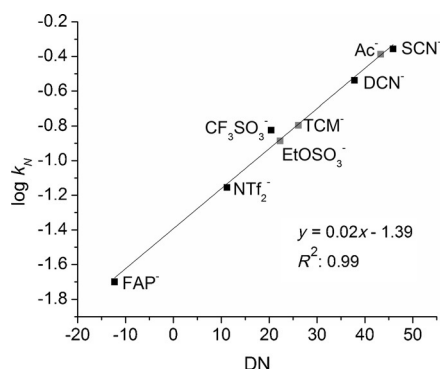


Figure 1. Comparison between $\log k_N$ and DNs for the series of $[\text{EMIM}]^+$. Red squares represents points predicted from Equation (2).

Table 1, this anion is bigger than the Ac^- anion. Other predictions can be made with comparable consistency.

To close the discussion based on Gutmann's numbers, we performed an additional comparison between the recorded k_N coefficients and the AN. The result of this comparison is depicted in Figure 2.

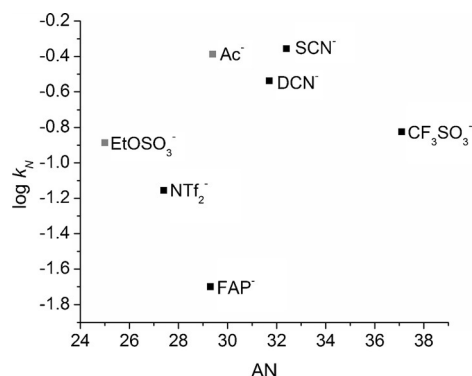


Figure 2. Comparison between $\log k_N$ and ANs for the series of $[\text{EMIM}]^+$.

It may be observed that the correlation between $\log k_N$ and Gutmann's AN is very poor, thereby reinforcing the argument that the anion outweighs the cation solvent effect within the series of ILs considered in this study. Note further that the comparison between the β parameter with the DN does give a nice linear relationship, a result that closes the argumentation in favor of an "anion solvent effect" in these systems (see Figure 3).

Conclusion

We have presented an experimental study to discuss the effect of the solvent on a model $\text{S}_\text{N}\text{Ar}$ reaction in a series of pure ILs. A significant catalytic effect is observed with reference to the same reaction run in water, acetonitrile, and other conventional solvents. The observed solvent effects can be attributed to an "anion effect". The anion effect appears to be related to the anion size (polarizability) and its hydrogen-bonding (HB) abilities to the substrate. We first performed comparisons between rate constants and KT solvatochromic parameters. The statisti-

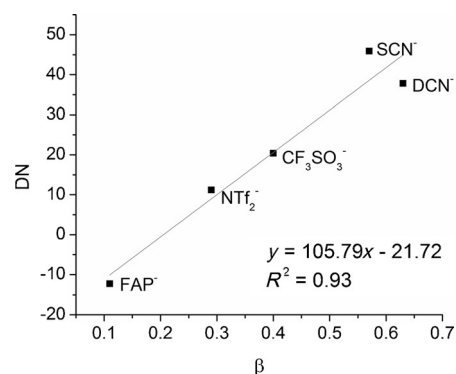


Figure 3. Comparison between DN and β for the series of $[\text{EMIM}]^+$.

cal analysis including the three KT parameters consistently failed. However, when rate coefficients for the model reaction were compared with Gutmann's donicity numbers, a remarkable linear correlation was obtained. The resulting empirical linear equation was used to predict the rate coefficients of three ILs not included in the correlation and sound results were obtained, which are consistent with the kinetic data recorded.

Experimental Section

Kinetic measurements

These were carried out spectrophotometrically (330–500 nm) by means of a diode array spectrophotometer with a series of ionic liquids based on the imidazolium and pyrrolidinium cations at $25 \pm 0.1^\circ\text{C}$. The reactions, studied under excess of the amine compared with the substrate, were started by injection of a substrate stock solution in the IL into the amine solution in the IL (1000 μL in the spectrophotometric cell). Under these conditions, pseudo-first-order rate coefficients (k_{obs}) were found. The rate coefficient values for morpholine (k_N) were obtained from plots of k_{obs} versus [amine]. The experimental conditions of the reaction and the k_{obs} values are listed in Figures S1–S15 and Tables S1–S7 in the Supporting Information.

Determination of solvatochromic parameters

The solvent parameters was measured by injecting the 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 min). The concentration of the stock solution was $1.85 \times 10^{-3} \text{ M}$. All the solutions was thermostated at $25 \pm 0.1^\circ\text{C}$.

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) $< 0.1\%$.

Product analysis

The presence of *N*-(2,4-dinitrophenyl)morpholine as the product of the model reaction was determined spectrophotometrically by comparison of the UV/Visible spectra at the end of the reactions with those of authentic samples under the same conditions.

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Keywords: anion (solvent) effects • Gutmann's donicity numbers • ionic liquids • Lewis acidity/basicity

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