Conference paper

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An efficient and eco-friendly method for the thiol-Michael addition in aqueous solutions using amino acid ionic liquids (AAILs) as organocatalysts

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Abstract: A series of amino-acid based ionic liquids (Bmim[AA]s) have been synthesized and evaluated as catalysts, in aqueous solution. The results of a kinetic study of the thiol-Michael reaction of L-Cysteine with *trans*-β-nitrostyrene demonstrated the advantages of using (Bmim[AA]s) as organocatalysts. The benefits include high rate constants; mild reaction conditions; and, a reusable catalyst, which leads to a simple and efficient method for these important kinds of reactions.

Keywords: amino acid ionic liquids; ICPOC-24; organocatalyst; thiol-Michael reaction; *trans*-β-nitrostyrene.

Introduction

Currently, organocatalysts have attracted enormous interest in diverse fields of chemistry owing to their simplicity, low toxicity and environmentally benign nature compared to metal and heterogeneous catalysts [1–4]. Accordingly, List *et al.* described the first example of a nonmetallic small-molecule catalyst for direct intermolecular asymmetric aldol reactions, using L-proline as an organocatalyst [5]. The benefits of L-proline as an organocatalyst in these kinds of reactions are that they do not require inert conditions, they can usually be performed at room temperature, the catalyst can be readily removed, and finally, its effect is comparable to the best organometallic catalysts [6, 7]. Since the work of List *et al.*, amino acids (AA) have played an important role in organocatalysis [8–10]. In particular, L-proline and its derivatives have been established as versatile catalysts for a variety of reactions including Michael addition [11–18].

In many cases however, the direct use of an amino acid as a catalyst has not promoted the reaction as expected, because of its limited solubility in conventional organic solvents (COS) [19–21]. This drawback can be effectively solved when the amino acid is included as a cation or anion of an ionic liquid (IL). This kind of IL's are called amino acid ionic liquids (AAILs) [22–25]. AAILs are miscible with various COS, such as methanol, acetonitrile, chloroform, and even more so in water [26–28]. In addition, it is important to mention that AAILs have "green" properties given that they are biodegradable [29–31] and could be less toxic than conventional ILs with anions such as bistrifluoromethylsulfonyl, tetrafluroborate and hexafluorophosphate due to their hydrolytically unstable properties [32, 33]. An example of AAILs used as an organocatalyst for Michael addition is the work of Wang *et al.*, in which they utilized 1-ethyl-3-methylimidazolium prolinate as

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an organocatalyst for the reaction of cyclohexanone with various substituted chalcones [34]. The reaction afforded Michael adducts in high yields and relatively good enantioselectivities. Nevertheless, a high loading catalyst (200 mol %) was required and the use of COS was necessary to do the reaction. On the other hand, Pernak *et al.*, utilized ammonium L-prolinates as an organocatalyst for the Michael addition with ketone to nitrostyrene in dichloromethane [35]. Their results demonstrated that ammonium L-prolinates are a more efficient catalysis in comparison to those obtained when L-proline was used as an organocatalyst.

Other authors have also reported the use of different AAILs in carbon and aza-Michael reactions [36–38] however, only a few studies related to the thiol-Michael addition have been reported [39]. An interesting study on the thiol-Michael reaction, is the efficient conjugate addition of thiophenol to sulfonamide chalcones using L-proline nitrate as an organocatalyst. This methodology showed benefits such as mild reaction conditions, operational simplicity and high yields, but the use of acetonitrile was necessary to do the reaction. Nevertheless, it is desirable that the catalysis can be performed in water, with the aim to the develop more environmentally friendly chemical processes [40–43].

Considering the above, we proposed herein, for first time a detailed kinetic study of a thiol-Michael reaction using AAILs as an organocatalyst, in aqueous solutions. To this end, the reaction of L-Cysteine (L-Cys) with *trans*-β-nitrostyrene (**1**) was chosen as a model of thiol-Michael addition using a series of amino acid based ionic liquids containing 1-butyl-3-methylimidazolium (Bmim[AA]) as an organocatalyst. This series involves different amino acids as anions, such as L-histidine, L-alanine, L-phenylalanine, L-asparagine, L-serine, L-methionine, L-proline, and glycine, providing different structures and chemical properties, which may be important for rationalizing the catalytic effect in the studied reaction.

Experimental section

Reagents and materials

All aminoacids (AA), *trans*-β-nitrostyrene (**1**), Amberlite IRA400Cl were of high quality and were used as received without further purification. 1-Butyl-4-methylimidazolium chloride Bmim[Cl] was purchased and decolorized with an activated charcoal powder and dried in a vacuum at 80 °C for 2 days.

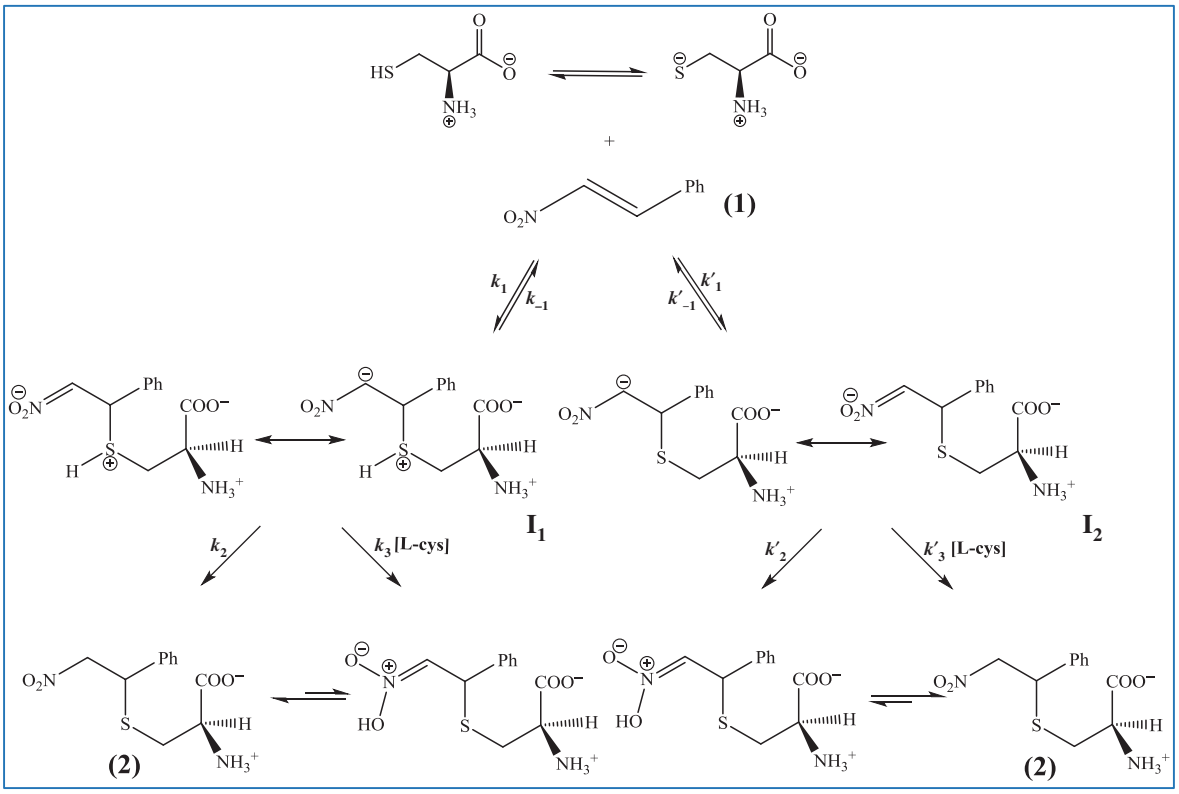
Synthesis and characterization

The amino acid based ionic liquids (AAILs) were synthesized by the methodology reported by Ohno *et al*. The synthesis of these Bmim[AA] involved two steps. First, an ion exchange reaction of Bmim[Cl] with amberlite as an anion exchange resin to obtain Bmim[OH]. Second, the neutralization of the amino acid by Bmim[OH] [44] (see Scheme S1 in SI). Eight Bmim[AA]s have been synthesized in this work and their structure was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS-ESI in accordance with what is reported in the literature [45–48]. It is important to note that the water content for each Bmim[AA] was ~7–10 wt % and was determined by Karl Fisher Titration (TitroMatic).

The Michael adduct was synthesized by a modified methodology [49]. Acetonitrile was used instead of methanol and the reaction was carried out in the absence of potassium acetate (see NMR spectra and HRMS-ESI spectra in Figs. S1–S5 in SI). The Michael adduct was characterized by HRMS-ESI at the end of the reactions of **1** with L-cysteine in the same kinetic conditions using four different Bmim[AA]s (see Figs. S6–S9).

Kinetic measurements

These were performed spectrophotometrically in the 190–450 nm range by following the disappearance of **1** (at 320 nm) after at least four half-lives, by means of a Hewlett-Packard 8453 instrument. In a typical



Scheme 1: Proposed mechanism for the reaction between **1** and L-Cys.

spectrophotometric measurement, a quartz cuvette (light-path 1 cm) containing 2000 µL of aqueous solution of L-Cys in a 5×10^{-5}–5.5×10^{-3} M concentration range at pH = 5.5 was thermostated at 25 ± 0.1 °C. Then, a solution of **1** (10 µL, 1×10^{-3} M in ACN) was added. The spectra were recorded at different reaction times and pseudo-first-order rate coefficients (k_{obsd}) were found for all reactions (see Table S1 in SI).

The second order rate constant (k_N) was obtained from the slope of a k_{obsd} against a total L-Cys concentration plot.

In addition, the catalytic constants (k_{cat}) of Bmim[AA] were determinated. For this purpose, 2000 µL of aqueous solution of L-Cys 5×10^{-4} M and the variable concentration of Bmim[AA] (5×10^{-6}–3×10^{-5} M) was thermostated at 25.0 ± 0.1 °C. Then, a solution of **1** (10 µL, 1×10^{-2} M in ACN) was added. The spectra were recorded at different reaction times and pseudo-first-order rate coefficients (k_{obsd}) were found for all reactions (see Table S2 in SI). The slope of linear plots of k_{obsd} vs. Bmim[AA] concentration showed the second order rate constants (k_{cat}) for the eight Bmim[AA]s that were obtained.

For the temperature dependence studies, the reaction was done in the absence and in the presence of different Bmim[AA] under the same experimental conditions mentioned above. The temperature range used was 9–32 °C (see Tables S1–S4 in SI).

Reusability study

A reusability study was realized for all Bmim[AA]s. For this purpose, in a spectrometric cuvette, 2000 µL of aqueous solution of [L-Cys] = 7×10^{-4} M and Bmim[AA] 2.5×10^{-5} M was thermostated at 25.0 ± 0.1 °C. Then, 10 µL solution of **1** (1×10^{-2} M in ACN) was added to start the reaction. The kinetic was followed by UV-vis (at 320 nm) and pseudo-first-order rate coefficients k_{obsd} were obtained. Then, in the same cuvette, 1 µL of L-Cys (1×10^{-1} M) was added to replace the quantity of L-Cys consumed in the preceding cycle. Then, a new cycle

was begun with the addition of 1 μL of **1** (1×10^{-1} M in ACN) and so on until a k_{obsd} was obtained for each cycle of the study (each sample was done in triplicate). The k_{obsd} values obtained in each cycle are shown in Table S5, in SI.

Results and discussion

With the aim of evaluating the effect of Bmim[AA] ionic liquids as catalysts for the reaction of **1** with L-Cys as a nucleophile, a kinetic study was performed in aqueous media, pH 5.5 at 25.0 ± 0.1 °C. In order to understand the mechanism reaction of **1** with L-Cys, as a Michael model reaction in water without a catalyst, the kinetic study was performed under the same experimental conditions.

For this purpose, all reactions were performed under pseudo-first-order conditions. The rate constant values (k_{obsd}) and the experimental conditions of all the reactions are summarized in Table S1 in SI.

Considering the presence of two nucleophilic groups in L-Cys (sulfhydryl and amino groups), the second order nucleophilic rate constants (k_N) for the reaction of **1** with N-acetyl cysteine (NAC) and D-penicillamine (Pen) were determined, in the same experimental conditions, as control experiments. In these cases, only one of the nucleophilic group is present. As shown in Table S6 in SI, similar k_N values were obtained when NAC was used as a nucleophile. However, the k_N value for Pen is almost one order of magnitude lower than that obtained with L-Cys. The later suggest that the thiol group of the L-Cys is the responsible of the nucleophilic attack on **1**. In addition, to corroborate the later, we have synthesized and characterized the thiol-Michael adduct (**2**, in Scheme 1) obtained in this kinetic study, see Figs. S1–S4, in Supporting information.

Reaction in the absence of catalyst

pH effect

A study of the kinetic reaction of **1** with a constant concentration of L-Cys (5×10^{-4} M) shows a dependence of pH (see Table S7 in SI). This dependence on k_{obsd} is a consequence of the fraction of thiol and thiolate free (F_N^{SH} and $F_N^{S^-}$, respectively). The kinetic effect of the presence of thiol and thiolate can be separate as shown in eqs. 1–3.

$$k_{obsd} = k_0 + (k_{S^-} F_N^{S^-} + k_{SH} F_N^{SH})[\text{L-Cys}]_T \quad (1)$$

$$k_{Nobsd} = k_{S^-} F_N^{S^-} + k_{SH} F_N^{SH} \quad (2)$$

$$\frac{k_{Nobsd}}{F_N^{SH}} = k_{SH} + k_{S^-} \frac{F_N^{S^-}}{F_N^{SH}} \quad (3)$$

The k_{obsd} considers the three reactions that **1** can suffer in the reaction medium. These are, first, hydrolysis by solvent (k_0); second, nucleophilic attack by free thiolate; and, finally, nucleophilic attack by thiol groups of L-Cys. The terms k_{S^-} and k_{SH} are the nucleophilic rate coefficients for each reactive species of L-Cys, and $F_N^{S^-}$ and F_N^{SH} the corresponding fractions of free thiolate and thiol, respectively.

It is important to note that the rate constant value for the hydrolysis of **1** have been reported previously as $k_0 = 8.5\times10^{-7}$ s^{-1} at pH 5.2 [50], which is considerably lower than the k_{obsd} values obtained in this study. Thus, the k_0 value is insignificant and not considered in this study.

Therefore, taking into account the kinetic results obtained at different pH values by using eq. 3, a linear plot of $\frac{k_{Nobsd}}{F_N^{SH}}$ vs. $\frac{F_N^{S^-}}{F_N^{SH}}$, was obtained (Fig. 1).

From the slope and intercept of Fig. 1, the constants: $k_{s^-} = 6010 \pm 455\ s^{-1}\ M^{-1}$ and $k_{SH} = 29.3 \pm 4.4\ s^{-1}\ M^{-1}$ were obtained, which indicate that both species (thiolate and thiol of L-Cys) act as nucleophiles in the studied reaction. Thus the contribution to k_{obsd} value of both species of L-Cys is relevant.

L-Cys concentration effect

The dependence of the k_{obsd} values vs. $[L\text{-}Cys]_T$ was assessed for the reaction of **1**. As we can see in Fig. 2, there are two different behaviors. First at low L-Cys concentration it curves up, which obeys a parabolic behavior, with a first and a second order in L-Cys. Second, at high L-Cys concentrations a linear behavior, which follows a first order kinetic behavior in L-Cys.

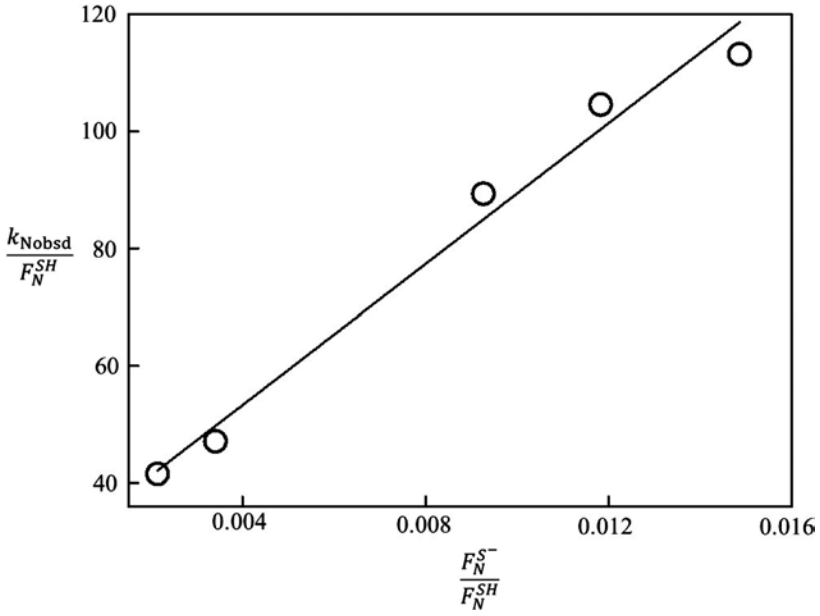


Fig. 1: Graphic representation of kinetic data fitting to eq. 3.

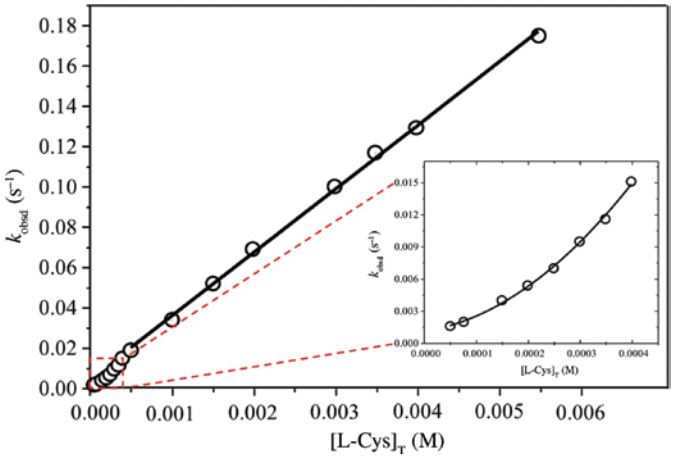


Fig. 2: Plot k_{obsd} against $[L\text{-}Cys]_T$ for thiol-Michael studied reaction of **1** (5×10^{-6} M) and L-Cys (5×10^{-5}–5.5×10^{-3} M) range in aqueous solution (pH 5.5) at 25.0 ± 0.1 °C.

The kinetic behavior of the title reaction is consistent with the mechanism proposed in Scheme 1. In this scheme at high concentrations of [L-Cys], α-carbon's protonation in intermediates I_1 and I_2 are fast and the determining step rate is the nucleophilic attack of both species of L-Cys (S^- and SH) toward β carbon of **1**. On the other hand, at low [L-Cys] concentrations, the second order contribution could be explained by the participation of a second L-Cys molecule in the α-carbon's protonation in intermediates I_1 and I_2 (k_3 and k'_3 steps, respectively). In addition, the first order evidence of low L-Cys concentration can be explained through an intramolecular proton transfer from I_1 (k_2) or by protonation of an intermediate I_2 by the medium (k'_2).

Applying the steady-state conditions to intermediate I_1 and I_2 of Scheme 1, eq. (4) was obtained.

$$k_{obsd} = \frac{k_1[\text{L-Cys}]_T(k_2 + k_3\,[\text{L-Cys}]_T)}{k_{-1} + k_2 + k_3[\text{L-Cys}]_T} + \frac{k'_1[\text{L-Cys}]_T(k'_2 + k'_3\,[\text{L-Cys}]_T)}{k'_{-1} + k'_2 + k'_3\,[\text{L-Cys}]_T} \quad (4)$$

For the reactions of **1** with low L-Cys concentrations ($k_{-1} > k_2 + k_3\,[\text{L-Cys}]_T$ and $k'_{-1} > k'_2 + k'_3\,[\text{L-Cys}]_T$), and $k_{obsd} = (K_1k_2[\text{L-Cys}] + k_3\,[\text{L-Cys}]^2_T) + (K'_1K'_2[\text{L-Cys}] + k'_3\,[\text{L-Cys}]^2_T)$ where K_1 and K'_1 are the equilibrium constant of the first step ($K_1 = k_1/k_{-1}$ and $K'_1 = k'_1/k'_{-1}$) and a first and second order in L-Cys was observed. This is in accordance with a parabolic representation (see insert in Fig. 2). On the other hand, at higher L-Cys, eq. 4 reduces to eq. 5 where linear plots (k_{obsd}) vs. $[\text{L-Cys}]_T$ were obtained, and the first one is the rate determining step.

$$k_{obsd} = (k_1 + k'_1)[\text{L-Cys}]_T \quad (5)$$

It is interesting to note that the sum of $k_1 + k'_1$ value obtained from the slope of the linear portion is an apparent value. This is because it is at one constant pH value.

On the other hand, it is important to mention that an apparent second order rate constant of 45 M^{-1} min^{-1} (0.75 M^{-1} s^{-1}) for a reaction of L-Cys with *trans*-β-nitrostyrene, have been reported by other authors under different experimental conditions [sodium acetate buffer pH 4 ethanol (8:2, v/v) mixture]. Considering these differences, with particular regard to the reaction media (pH, thiolate fraction and lower polarity solvent), the apparent nucleophilic rate constant (k_1) value obtained in this study from Fig. 2 (31.6 ± 0.45 M^{-1} s^{-1}) is consistent with the bibliographic value.

Reaction in the presence of catalyst

For the first time a robust kinetic treatment for thiol-Michael addition, in the presence of Bmim[AA]s as catalysts, have been performed. In particular, it was done in the presence of varied concentrations of different Bmim[AA]s and at fixed $[\text{L-Cys}] = 5 \times 10^{-4}$ M. Experimental conditions of all the reactions and the k_{obsd} values are summarized in Table S2 in SI. As an example, Fig. 3 shows the plots of k_{obsd} vs. Bmim[AA] where [AA] = His, Ser and Gly. From the slope of these plots the apparent rate constants for the nucleophilic reaction in the presence of the catalyst, k_{cat} values have been obtained and are shown in Table 1.

Table 1 summarizes the second order catalytic rate constants (k_{cat}) obtained from the slope of the k_{obsd} vs. the catalyst concentration. These k_{cat} values obtained in the presence of each Bmim[AA] are in the range of 700–1700 M^{-1} s^{-1}. Furthermore, these catalytic rate constants are more than one order of magnitude higher than that obtained in the presence of (Bmim[Br]). The latter, seems to prove that the catalytic effect of the cation is low and could only be due to the IL anion. In addition, the title reaction in the presence of each amino acid alone has been performed. The results showed a negligible catalytic effect in comparison with that determined in the presence of the corresponding Bmim[AA].

The catalytic effect attributed to AA present in each Bmim[AA] could be associated with the activation of L-Cys from its thiol to its thiolate form. In particular, the amine group of the ionic liquid might assist in the formation of the nucleophilic anion of the thiol group, thereby increasing the nucleophilicity of L-Cys. The highest catalytic effect of the Bmim[AA] could be related with the hydrogen acceptor ability of the ionic liquid

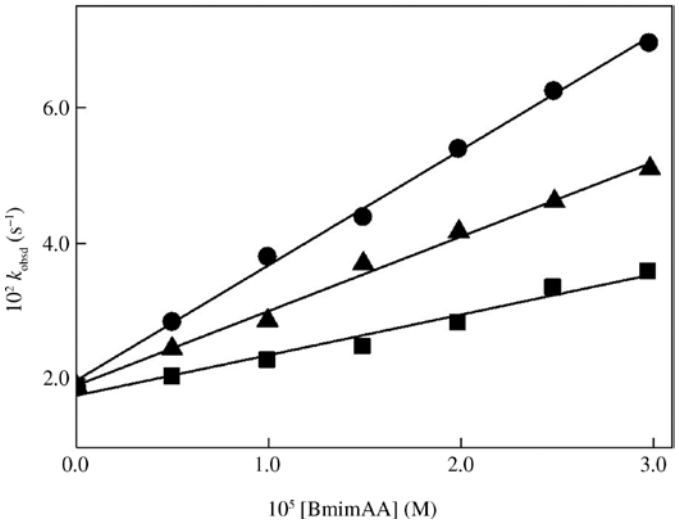


Fig. 3: Plot of k_{obsd} against [BmimHis] (●), [BmimSer] (▲) and [BmimGly] (■) for thiol-Michael studied reaction of **1** (5×10^{-5} M) and L-Cys (5×10^{-4} M) in aqueous solution (pH 5.5) at 25 °C ± 0.1.

Table 1: Catalytic rate constants (k_{cat}) for the title reaction in the presence of Bmim[AA] (0.5–3) $\times 10^{-5}$ M concentration range of catalyst) in H_2O at 25 ± 0.1 °C at pH 5.5.

Bmim[AA]	$k_{cat}/(M^{-1}\ s^{-1})$
Bmim[His]	1695 ± 39
Bmim[Ala]	1442 ± 104
Bmim[Phe]	1343 ± 53
Bmim[Asn]	1138 ± 70
Bmim[Ser]	1094 ± 40
Bmim[Met]	1094 ± 71
Bmim[Gly]	741 ± 59
Bmim[Pro]	698 ± 72
Bmim[Br]	9 ± 2

anion (AAs) (β parameter Kamlet and Taft reported in ref. [51]). Nevertheless, this trend was only found for those AAs structurally similar such as alpha-amino acids (L-Ala, L-Phe, L-Asn and L-Ser). In fact, a similar behavior has been established for other kind of nucleophilic reaction in the presence of Bmim[AA] [51] and for amino acid residues that affect the basicity of the catalytic glutamate in the presence of hydrolytic aldehyde dehydrogenases, acting as a general base activating the catalytic thiol [52].

Temperature effect

Temperature dependence studies of the title reaction in the absence and presence of Bmim[AA] were carried out in the temperature range 9–32 °C. The experimental conditions and the kinetics results are summarized in Tables S1–S4 in the SI. The activation parameters were determined by using Arrhenius and Eyring equations and are summarized below in Table 2.

As we can see in Table 2, in the absence of Bmim[AA] the studied reaction proceeds with a Gibbs free energy ($\Delta G^{\ddagger}$) barrier of 65 kJ mol^{-1}. Nevertheless, when the Bmim[AA] is present, a decrease of the barrier to 55–57 kJ mol^{-1} was observed. Therefore, the incorporation of Bmim[AA] in the reaction would imply a change in the nature of the transition states creating a catalytic effect.

Table 2: Activation parameters for the reaction of **1** with L-Cys in the absence and in the presence of Bmim[AA] used as a catalyst.

Catalyst	E_a (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
–	94 ± 8	92 ± 8	91 ± 9	65
Bmim[Ala]	67 ± 4	65 ± 4	32 ± 2	55
Bmim[Gly]	38 ± 4	35 ± 4	−73 ± 8	57
Bmim[His]	34 ± 2	31 ± 2	−78 ± 5	55
Bmim[Met]	76 ± 10	73 ± 10	60 ± 8	55
Bmim[Asn]	53 ± 5	51 ± 5	−17 ± 2	56

On the other hand, considering the enthalpy and entropy changes for title reaction in the presence of each Bmim[AA] used in this study (Table 2), a linear dependence between $\Delta H^{\pm}$ and $\Delta S^{\pm}$ was found, as shown in Fig. 4 ($r^2 = 0.9998$).

These dependence is known as enthalpy – entropy compensation (EEC) and is represented by the eq. 6.

$$\Delta H^{\pm} = a + b\Delta S^{\pm} \tag{6}$$

where "a" and "b" are constants. In particular, "a" has energy dimensions and it is associated with an activation free energy change ($\Delta G^{\pm}$). On the other hand the term "b" is the so-called "compensation temperature" (T_{comp}). Although this takes into account constraints mainly related to experimental uncertainties [53–55]. A previous study conducted by Perez-Benito [56] demonstrated from statistical analysis that kinetic EEC with $T_{comp} < T_{expt}$ is experimentally-error-based; however, they indicated that those with $T_{comp} > T_{expt}$ are thought to be real and meaningful by them. Nonetheless, as shown in Fig. 4, a value of $T_{comp} = 295$ K was obtained, which is close to the average of T_{expt} (294 K).

On the other hand, considering that the range of $\Delta G^{\pm}$ values presented in Table 2 for each Bmim[AA] is much smaller than the range of $\Delta H^{\pm}$, an exact EEC process with constant free energy change arises.

Reusability of catalyst

It is well known that the reusability of a catalyst is the key factor in determining whether it has a potential application. In this study the ability of each Bmim[AA] to be successively reused was evaluated. k_{obsd} is a

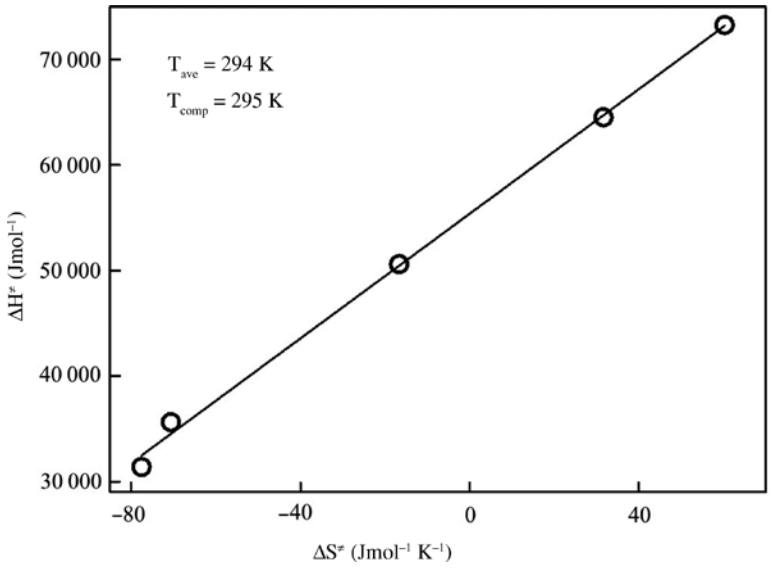


Fig. 4: $\Delta H^{\pm}$ vs. $\Delta S^{\pm}$ plot of the studied thiol-Michael reaction of **1** with L-Cys in the presence of different Bmim[AA]s.

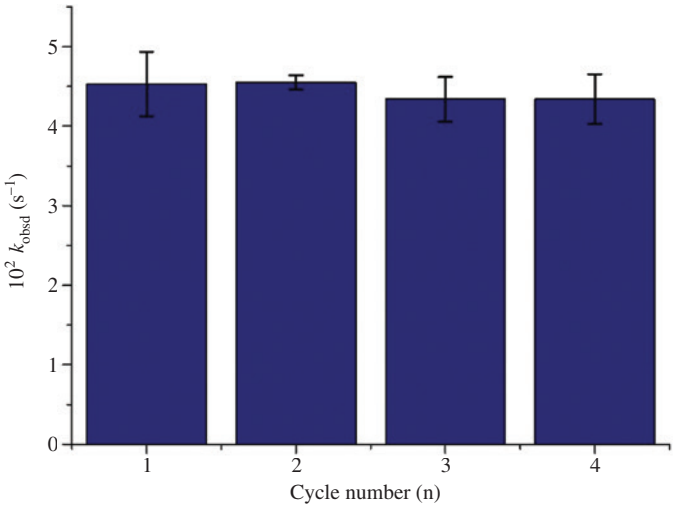


Fig. 5: Reusability of Bmim[Gly] (2.5×10^{-5} M) as catalyst for thiol-Michael reaction between **1** (5×10^{-5} M) and L-Cys (7×10^{-4} M) in aqueous solution (pH 5.5) at 25 °C ± 0.1.

pseudo first order constant of each successive cycle, Fig. 5 shows as an example the results obtained when Bmim[Gly] is used as a catalyst.

The results presented in Fig. 5 demonstrated that Bmim[Gly] could be reused up to four times while still maintaining its catalytic activity. The results obtained in the other Bmim[AA] depicted similar reusability, as shown in Table S5 in SI.

Conclusions

A series of amino acid based ionic liquids (AAILs) containing 1-butyl-3-methylimidazolium (Bmim) were synthesized and used as efficient organocatalysts for thiol-Michael addition of L-Cysteine to *trans*-β-nitrostyrene. The catalytic behaviour of the Bmim[AA]s would be associated with the AA present in each catalyst and its effect on the acid-base equilibrium (thiol-thiolate) of L-Cysteine.

These catalysts present several benefits such as high rate constants; mild reaction conditions; and, a reusability, which leads to a simple and efficient eco-friendly method for these reactions.

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