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## Review article

## Amino acid based ionic liquids: A green and sustainable perspective



Sarah Kirchhecker, Davide Esposito\*

Max Planck Institute of Colloids and Interfaces, 14424, Potsdam, Germany

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## ABSTRACT

Chiral and highly functionalized natural amino acids are readily available by renewable methods in high quantities. They can be easily converted into both anions and cations for the synthesis of ionic liquids. This mini review describes the synthesis of amino acid derived ionic liquids (AAILs) with a focus on the most recent developments. Some specialised applications for AAILs, namely in the fields of chiral solvents, acid catalysis and CO<sub>2</sub> absorption will be highlighted.

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## 1. Introduction

The past few decades have witnessed the rise of ionic liquids (ILs) as new green solvents, and many diverse uses have been suggested for this class of compounds [1,2].

Several of the ILs in standard use, such as the 1-alkyl-3-methylimidazolium type, however, are neither sustainable nor biodegradable, and in many cases exhibit relatively high toxicities [3]. On the other hand, biomolecules are generally biodegradable and many are non-toxic, as well as more sustainable than fossil resources. Therefore, the synthesis of ILs from biomolecules has an enormous potential to improve the green credentials of these very interesting compounds [4–6]. Many biomolecules can be incorporated into ILs, for example organic acids have been used as anions [7] and biological amines were derivatized as cations [8,9]. Amino acids (AAs) however have a special position amongst biomolecules as they can be easily converted into both anions and cations while the variety of functional groups present in their side chains enables the facile incorporation of chirality and a wide range of properties into the IL. Compared to the rest of the chiral pool, amino acids are cheap and abundant. AAILs have been around for just over 10 years. In this work very recent developments in the field will be highlighted, emphasising selected applications that can play a major role in the context of green and sustainable chemistry (Fig. 1).

## 2. Amino acids as anions

ILs with AA anions were first prepared by Ohno and coworkers in 2005 [10] by exposing ILs to an anion exchange resin for

conversion into hydroxides, which were then neutralised by combination with an equimolar amount of AA (Fig. 2A) [11]. All 20 natural amino acids were converted into IL anions in this way and resulted in room temperature ILs (RTILs). P<sub>4444</sub> cations in particular produced ILs of low viscosity and high thermal stability. This easy method of preparation has become the standard procedure to generate AA anion ILs. Following on from a previous report covering 5 AAILs [12], the Ohno group recently published a comprehensive study of the lyotropic liquid crystalline behaviour of an amphiphile in C<sub>4</sub>mim ILs containing the 20 different AA anions [13]. The authors showed that the temperature ranges of the mesophases as well as the isotropisation temperatures were different for each anion. These results point to the facile tuneability of the properties of AAILs by choice of their AA side chains.

Some fully biodegradable, non-toxic and potentially renewable ILs were produced by combining a choline cation ([Cho]) with AA anions (Fig. 2B). Choline is a constituent of cell membrane phospholipids. Currently manufactured from triethylamine and ethylene oxide, Cho may well be obtained from renewable sources in the future. Moriel et al. prepared five of these compounds by neutralising commercially available choline hydroxide with AAs [14], resulting in RTILs. The compounds were investigated as catalysts for the Knoevenagel condensation, where they all gave exclusively the *E* isomer, while the yields varied for different AA anions.

Liu et al. tested the dissolution of the biopolymers cellulose and lignin in [Cho][AA] ILs prepared by the same method [15]. Most of the 18 ILs tested could dissolve lignin at 90 °C at concentrations above 140 mg/g IL. Dissolution appeared to be enhanced by the alkalinity of the IL medium, while at lower temperatures the viscosity of the ILs had the most pronounced effect on dissolution. Cellulose on the other hand had very low or no solubility in these ILs, which prompted the authors to investigate them for biomass

\* Corresponding author.

E-mail address: [davide.esposito@mpikg.mpg.de](mailto:davide.esposito@mpikg.mpg.de) (D. Esposito).

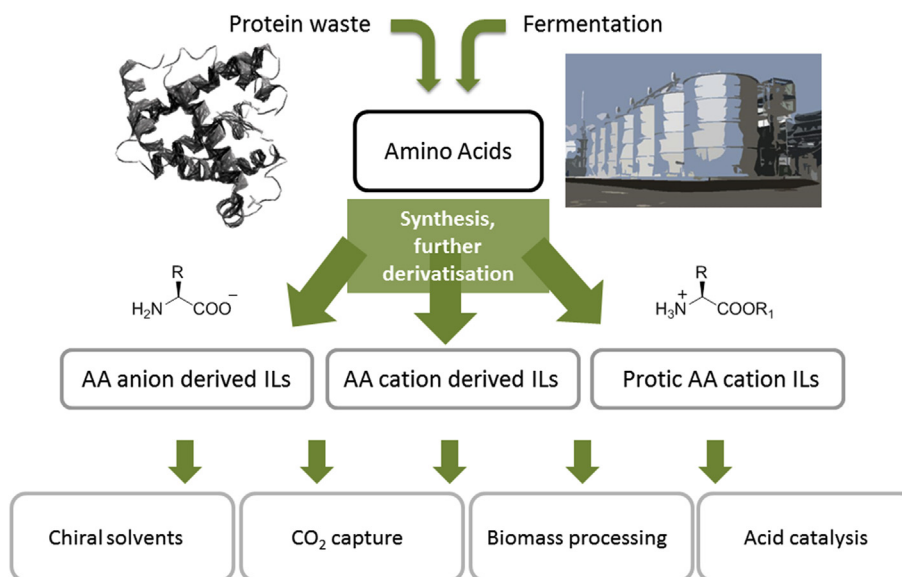
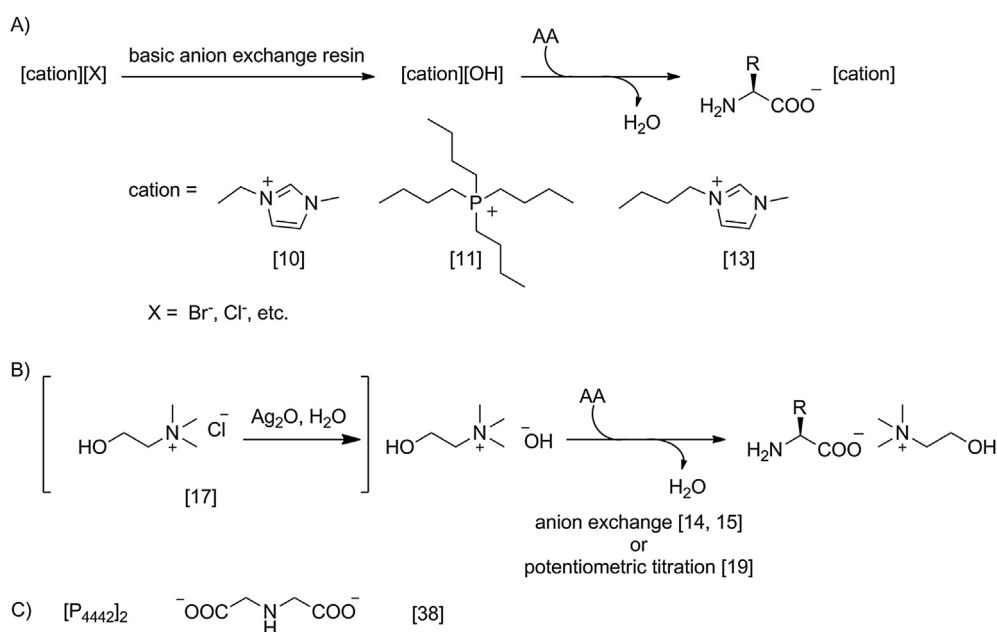


Fig. 1. Overview of topics covered in this review.



**Fig. 2.** IL anions derived from amino acids. A) Synthesis of AA anion ILs by anion exchange and some of the cations employed; B) Synthesis of [Cho][AA] ILs; C) modified AA anion for CO<sub>2</sub> absorption.

pretreatment. Choline glycinate was chosen due to its lower viscosity and employed for the pretreatment of rice straw. After 24 h of treatment with the IL, glucose liberation by cellulase was 7 times higher than without the pretreatment. Mu et al. assessed the use of lignin dissolved in [Cho][Gly] and [Cho][Pro] as bio-derived lubricants [16]. Reciprocal hydrogen bonding between the IL and lignin improved the thermal and frictional stability, and the materials were found to be non-corrosive to steel and aluminium.

An in depth study of the physicochemical properties of five [Cho][AA] ILs was published by Tao et al. [17]. The expected low toxicity and facile biodegradability of the fully bioderived [Cho][AA] ILs was confirmed in a recent study [18].

De Santis et al. developed a different synthesis of [Cho][AA] ILs employing potentiometric titration. This method is faster, avoids the use of organic solvent to precipitate the excess of AA and achieves high yields [19]. 18 different ILs were synthesised in this way, 14 of which were RTILs. The viscosities of these ILs were reported to be quite high, with the ones related to anions derived from AAs with alkyl chains being the lowest. Interestingly, the viscosity data showed good agreement with those recorded by Tao, while they were significantly higher than the values reported by Liu, in some cases by two orders of magnitude. This highlights the well-known dependence of ILs' viscosity on very small amounts of impurities or water.

### 3. Amino acids as cations

In analogy to the neutralisation reactions mentioned above, the simplest way to convert AAs into cations is by protonation with strong acids. Tao et al. produced many different ILs in this way (Fig. 3A) [20]. To reduce the possibility for hydrogen bonding the group also used AA methyl esters as the starting material, which led to ILs with lower melting points, in many cases producing RTILs. The degradation temperatures of these compounds were in the range of 150–200 °C.

Recently the  $pK_a$  values for AA derived protic ILs were determined by Zhang et al. for all 20 natural AAs combined with five different strong acid derived anions ( $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{TfO}^-$ ,  $\text{TFA}^-$ ,  $\text{ClO}_4^-$ ) [21]. Using potentiometric titration, the  $pK_a$  values were found to be in the range of 1.98–2.42, placing them between  $\text{HNO}_3$  and formic acid, as moderately strong acids. Comparison with esterified AAILs confirmed that the first  $pK_a$ s were due to the carboxyl group proton.

Li and Yang used protic proline derived ILs as a solvent/catalyst system for the conversion of fructose and sucrose into HMF. A yield of 73.6% from fructose was achieved with  $[\text{Pro}]\text{Cl}$  and the IL could be recycled five times with a very minor decrease in yield [22]. Protic AAILs were also used as acid catalysts in the esterification of valeric acid and ethanol to produce a new potential biofuel with a higher energy density than alcohols or  $\gamma$ -valerolactone [23].  $[\text{Pro}]\text{HSO}_4$ , the most acidic of the three AAILs tested, gave the best yield, with nearly quantitative formation of ethyl valerate after 7 h at 80 °C. In addition, while the starting materials as well as the water side product are soluble in the IL, the product separates out from the reaction mixture, allowing for easy workup. The water could be removed by heating and the IL reused for at least five times without obvious loss of catalytic activity.

While protic AAILs are useful as acid catalyst/solvent systems, for other applications more stable non-protic cations are required. Therefore most syntheses of AA derived cations require several steps.

In this area research mostly focuses on the alkylation of the amino groups of AAs. For example, Roshan et al. synthesised a range of AAILs by microwave assisted alkylation of AAs with methyl and ethyl halides and employed the resulting ILs in cycloaddition of  $\text{CO}_2$  to styrene oxide under atmospheric pressure [24]. Amongst these, an IL derived from the reaction of histidine methyl ester with methyl iodide (Fig. 3B) showed the highest activity with 95% conversion and 99% selectivity, due to the formation of a carbamate with the imidazole sidechain as a reaction intermediate.

In contrast, our group adopted a different approach, using the AAs as N-donors for the formation of N-heterocycles. To synthesise imidazolium compounds, zwitterions were formed at room temperature from two equivalents of amino acids, formaldehyde and methylglyoxal or glyoxal in a modified Debus-Radziszewski reaction (Fig. 3C) [25]. These compounds can be converted into acidic ILs by reaction with strong acids [26] or alternatively decarboxylated under hydrothermal conditions using a flow reactor in the presence of acetic acid to produce symmetrically N-substituted imidazolium ILs. Due to the chosen conditions these ILs are completely halide free and fully derived from renewable resources. This methodology was further extended to pyridinium cations which were produced by the hydrothermal decarboxylation of 3-hydroxy-pyridinium zwitterions synthesised from furfural and amino acids [27]. Besides acetic acid, other bioacids including lactic acid and succinic acid were also used during the hydrothermal step to produce anions. This way, bio-derived ILs with very similar properties to the well-established imidazolium and pyridinium type could be synthesised.

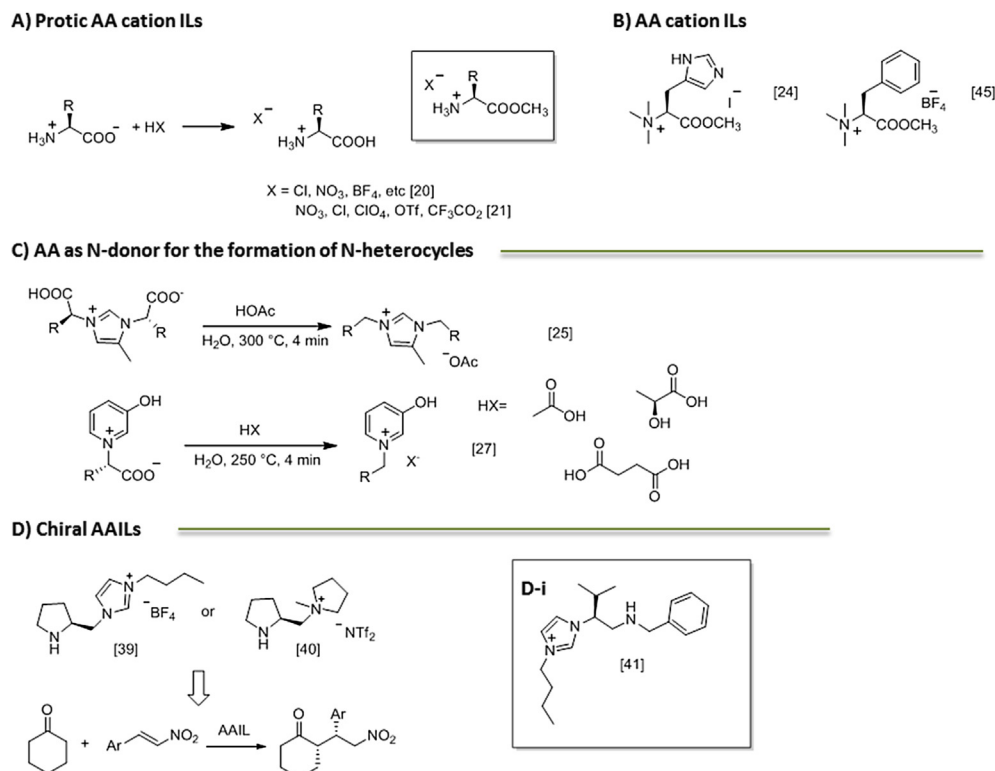


Fig. 3. IL cations derived from amino acids.

## 4. Applications

In analogy to their non-renewable counterparts, AAILs can be used for a variety of applications, including nanoparticle-catalysed Heck couplings [25,27], biomass pretreatment and acid catalysed esterifications, as mentioned above. Additionally, the unique structure of AAILs facilitates their use in some specialised applications.

### 4.1. CO<sub>2</sub> capture

Sequestration and recycling of anthropogenic carbon dioxide are important steps in the alleviation of global warming. Current technologies employ aqueous amine solutions [28], which absorb CO<sub>2</sub> at ambient temperature in a thermally reversible manner. These are cheap but have some drawbacks such as emission of VOCs and the high energy required for the stripping of CO<sub>2</sub>. More recently aqueous amino acid salts have been investigated, as well as amine-functionalised non-renewable ionic liquids [29]. However, for the latter compounds as well as the alkylamines CO<sub>2</sub> absorption is limited at 0.5 mol/mol amine due to a preferential 1:2 absorption mechanism (see Box 1). AAILs appear to be very suited to improve these capacities and several groups found higher than 50% absorption by AA anion ILs [30].

The Brennecke group reported a close to equimolar CO<sub>2</sub> absorption of proline and methionate phosphonium ILs, confirming with *ab initio* calculations that when the amine is located on the anion, the 1:1 absorption mechanism is energetically favoured [31]. In this case carbamic acid is formed preferentially over the carbamate, reflecting the energetic instability of a dianion.

Yang et al. quantified the mechanism of CO<sub>2</sub> absorption of several AA anion ILs with phosphonium cations by using a selective precipitation method [32]. While all AA anion ILs absorb more CO<sub>2</sub> than 0.5 mol/mol, some anions, including proline were found to absorb mainly in a 1:1 mechanism. The authors suggested that the strong intermolecular hydrogen bonding present helped to stabilise

the carbamic acid. In addition, they found a third absorption mechanism which contributed up to 25%. This was attributed to CO<sub>2</sub> binding via the carboxylate group.

The Riisager group synthesised tetraalkylammonium ILs with AA anions containing an extra amino group in their sidechains. [N<sub>66614</sub>][Lys] was able to absorb 2.1 mol CO<sub>2</sub>/mol IL at ambient temperature, and (partial) desorption was possible at elevated temperature (80 °C) in a CO<sub>2</sub> rich environment, suggesting that both amino groups react in the 1:1 mechanism. They also found that the ammonium lysinate IL had a higher absorption than the corresponding phosphonium IL, indicating some influence of the cation [33].

Chen et al. achieved a high CO<sub>2</sub> absorption of up to 1.69 mol/mol IL by N-substitution of glycinate anion with more carboxylates to decrease the negative inductive effect of the nitrogen and therefore increase the basicity of the carboxylates [34] (Fig. 2C).

The favoured absorption mechanisms and conformations of AAILs upon CO<sub>2</sub> binding were studied theoretically by first principles methods. It was found that most AAILs favour the 1:1 mechanism with a preferred *trans* conformation of the carbamic acid, which is responsible for the large increase in viscosity after absorption [35].

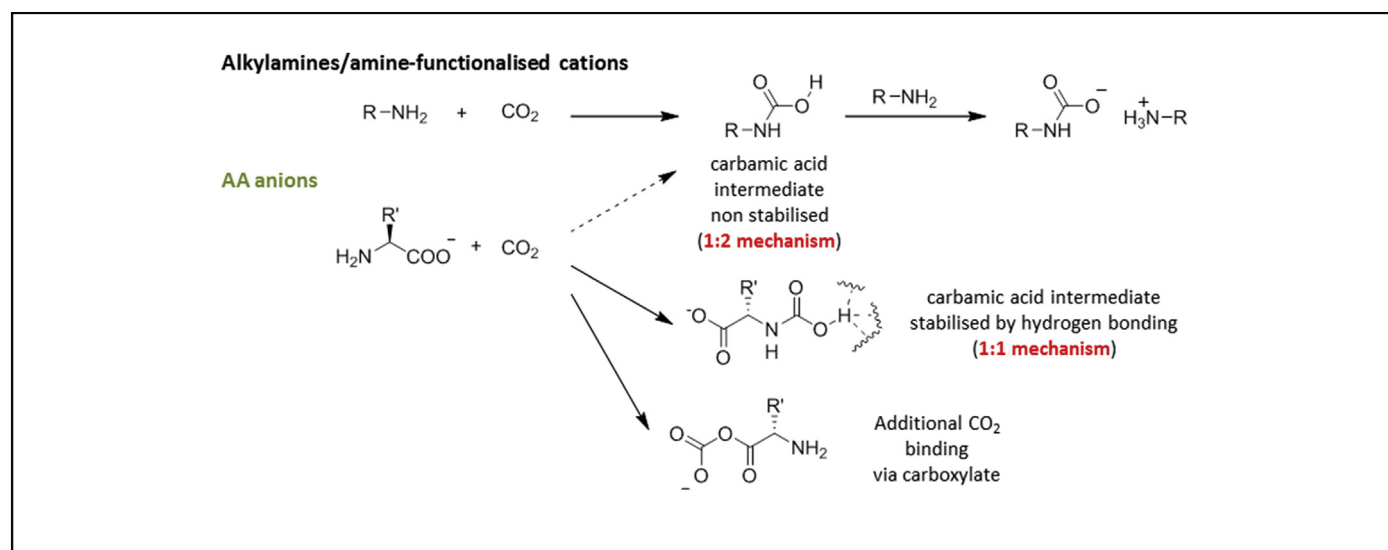
### 4.2. Exploitation of chirality

AAILs constitute a diverse and sustainable pool of chiral solvents for application in catalysis and material synthesis.

L-Proline is the archetypal organocatalyst, and since its first use in asymmetric aldol reactions [36], it has been investigated widely, including in IL solvents [4]. Generally, prolines have been either used as the chiral anion [37] or tethered to different standard IL cations [38]. A butyl-imidazolium-proline cation gave quantitative yields with *syn:anti* selectivity of 99:1 and an *ee* of 99% for the asymmetric Michael addition of cyclohexanone to *trans*-β-nitrostyrene (Fig. 3D) [39]. The same reaction was tested with a proline-pyrrolidinium IL recently, giving a slightly lower yield and selectivity [40].

### Box 1

Different CO<sub>2</sub> absorption mechanisms. The relative contribution of the two amine mediated paths to the overall absorption process depends on the level of stabilization of the intermediate carbamic acid, which is usually higher for AA anions.





Gonzalez et al. used AA amide-derived chiral ILs in combination with proline to catalyse the asymmetric aldol reaction between nitrobenzaldehyde and acetone (Fig. 3D–i). Using an imidazolium bistriflimide IL that contained a valine-derived amino amide as the second arm, high conversion and selectivity with an *ee* of 77% were achieved [41]. Using the non-natural AA (*R*)-proline, the authors found that a mismatch between the chirality of the AA IL medium and the proline catalyst affected the yields negatively. The same group also synthesised dimers of their AA-imidazolium salts for chiral anion recognition, where some enantioselectivity was achieved [42].

An area of research where chiral AAILs are expected to play an important role in the future, is the generation of chiral porous materials. While the application of ILs to the preparation of carbon materials has been well documented [43,44], only recently Fuchs et al. prepared for the first time chiral nanoporous carbons by salt melt carbonisation of AAILs [45]. The chiral ILs were synthesised by full methylation of AA methyl esters with iodomethane followed by anion exchange with NaBF<sub>4</sub> (Fig. 3B). Carbon materials prepared from either L- or D-phenylalanine derived ILs showed preferential adsorption of amino acids of the same chirality. While it is still a bit unclear how the chirality is preserved at carbonisation temperatures of 500 °C, the authors suggest that it may be due to stabilising effects of the zinc ions present in the salt melt.

## 5. Conclusion and outlook

In summary, this article reviewed the most recent developments in the field of AAILs. The use of AAs offers a sustainable alternative for the synthesis of ILs characterised by low toxicity and high biodegradability, which are very important features for “green” ILs. In addition, AAILs show a high potential for application in the field of green and sustainable chemistry. In this direction, examples in the areas of CO<sub>2</sub> capture, biomass processing and benign chiral catalysis have been provided. One of the biggest challenges for the industrial application of this class of compounds comes from the availability of cheap amino acid sources. Biotechnological production routes exist for many AAs due to their use as food and feed supplements [46,47], and large quantities of underutilised waste from the food industries and biorefineries are available. While at present efficient separation technologies for the constituent amino acids are still expensive for large scale implementation, progress in the field of enzymatic [48], biotechnological [46,49] and electrodialysis separation methods, including hybrid techniques, are expected to facilitate rapidly the procurement of amino acids as starting materials for the synthesis of AAILs.

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