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Full Paper

Protic Ionic Liquids Based on Oligomeric Anions $[(HSO_4)(H_2SO_4)_x]^-$ ($x = 0$, 1, or 2) for a Clean ε-Caprolactam Synthesis*

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Inexpensive Brønsted acidic ionic liquids, suitable for industrial-scale catalysis, are reported as reaction media and catalysts for the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. A family of protic ionic liquids was synthesised from nitrogen bases (1-methylimidazole, *N,N,N*-triethylamine, *N*-methylpyrrolidine, 2-picoline) and sulfuric acid by proton transfer in a simple, inexpensive, solvent-free, one-step process. The density, viscosity, conductivity, and ionicity of the synthesised ionic liquids were determined. Variation in the molar ratio of sulfuric acid ($\chi_{H_2SO_4} = 0.67$ and 0.75) was used to tune the acidity of these protic ionic liquids, which showed extremely high catalytic activity in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. Both the structure of the cation and the sulfuric acid molar ratio strongly affect the rearrangement of cyclohexanone oxime. The most active ionic liquid, based on the 1-metyhylimidazolium cation, $\chi_{H_2SO_4} = 0.75$, afforded high conversion of oxime combined with very good selectivity under mild conditions (110°C, 15 min). The product could be extracted from the reaction mixture, eliminating the need for the neutralisation step that exists in conventional processes. The combination of affordable catalyst and process advantages leads to a greener alternative, competitive against existent industrial applications.

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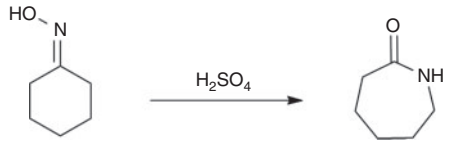
Introduction

High-performance polyamides are engineered thermoplastic materials that exhibit excellent strength, high chemical resistance, and high dielectric strength. They are synthesised from ε-caprolactam and adipic acid. ε-Caprolactam is the precursor of Nylon 6, which is a key component in the automotive, electrical, textile, and medical industry. The estimated world consumption for this monomer reaches over 5 million tons per year and is continually increasing, with estimates reaching 7 million tons in 2024.[1] Industrial production of ε-caprolactam is realised by the acid-catalysed Beckmann rearrangement of cyclohexanone oxime (Scheme 1).[2]

In order to achieve the complete conversion of cyclohexanone oxime to ε-caprolactam with high selectivity (99.5 %), an excess of oleum is required as the catalyst. The dissolved sulfur trioxide reacts with caprolactam to form the caprolactamium hydrogen sulfate salt, which is in fact an ionic liquid (IL), stable up to 140°C and provides a safe environment for a very exothermic reaction, thanks to its very low vapour pressure.[3] The major drawback of this process is the need to neutralise the reaction mixture with ammonia, in order to produce the final product. This step generates large amounts of $(NH_4)_2SO_4$ as a low-value by-product, which can be sold as a fertiliser. The neutralisation is unavoidable, and the formation of ammonium sulfate hampers the full recovery of the high-value product, ε-caprolactam, incurring a 10–15 % loss.[4]



Scheme 1. Beckmann rearrangement of cyclohexanone oxime.

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ILs have long been studied as alternative solvents for the Beckmann rearrangement, often used in a dual role of solvent and catalyst when bearing the acidic function in the cation or anion. Their main advantage was avoiding the formation of $(NH_4)_2SO_4$ by eliminating the neutralisation step. The first report dates back to 2001, when 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], was used under mild conditions in the presence of phosphorylated compounds or Eaton reagent to produce ε-caprolactam with high conversion (> 99 %) and high selectivity (> 99 %), but with a drawback of a very long reaction time (21 h).[5,6] The combination of metaboric acid in [bmim][PF_6] resulted in the reaction time being reduced to 3 h.[7] The Beckmann rearrangement was also performed using Lewis acids ($AlCl_3$, $TiCl_4$, $SnCl_4$, and BF_3) in ILs (1-butyl-3-methylimidazolium, 1-heptylpyridinium, and tetrabutylammonium bromides), leading to high conversions (up to 100 %) and selectivities (up to 100 %).[8,9] Very recently, mixed metal double salt ILs comprised of triethylammonium tetrachlorozincate and $AlCl_3$ revealed significant activity in a Beckman rearrangement of acetophenone oxime (conversion: 100 %, selectivity: 97.2 %).[10]

In 2004, new family of task-specific ILs were for the first time used in a dual role of solvent and acid catalyst in a Beckmann rearrangement.[11,12] An IL with sulfonyl chloride functionality gave full conversion of cyclohexanone oxime within 2–5 h, depending upon the reaction temperature and IL-to-substrate ratio. In addition, the investigated 1-(3-chlorosulfonylpropyl)-3-ethylimidazolium hexafluorophosphate was immiscible with water, affording ε-caprolactam separation from the reaction system by simple water extraction. It was the first example of a facile separation of ε-caprolactam from an IL. Unfortunately, the attempts to reuse the IL in the next reaction cycle resulted in a drastic drop of the cyclohexanone oxime conversion (34 %). Other studies used ILs based on 1-methylimidazolium, $[Hmim]^+$ and *N,N,N,N*-tetramethylguanidinium, $[tmg]^+$, cations as solvents and/or promoters.[13]

Brønsted-acidic ILs bearing a sulfonic acid group (-SO_3H) have been extensively studied as catalysts for ε-caprolactam transformations, for example in the one-step synthesis of ε-caprolactam from cyclohexanone and hydroxylamine.[14] The combination of sulfonated ILs with either $ZnCl_2$ or phosphotungstate was investigated in both the Beckmann rearrangement of cyclohexanone oxime[15–17] and direct synthesis of ε-caprolactam from cyclohexanone.[18] With respect to the Beckmann rearrangement, the best results reported so far were achieved using an aprotic IL with a $[HSO_4]^-$ anion and a sulfonic acid appended to the alkyl chain of the cation, in a dual role of both the solvent and the catalyst.[19] In the presence of this Brønsted acidic IL, ε-caprolactam was afforded with high selectivity and yield (> 99 %) within 4 h. In addition, the IL was successfully reused over four reaction cycles, without activity decrease. However, the price of this task-specific IL, prepared via several steps using an expensive sultone precursor, is much higher than the conventional oleum catalyst, and the reaction time required for full conversion (4 h) is much longer compared with the conventional process (15 min).

In contrast to highly efficient but expensive ILs with a sulfonic acid functional group, protic ionic liquids (PILs) prepared from nitrogen bases and variable quantities of Brønsted acids are inexpensive and highly tuneable, offering easy access to highly acidic systems.[20–24] In particular, combinations of nitrogen bases and an excess of sulfuric acid were found to be both inexpensive and highly Brønsted acidic, suitable for industrial-scale catalysis.[25,26] The excess of sulfuric acid leads to the formation of anionic clusters, $[(HSO_4)(H_2SO_4)_x]^-$ ($x = 1$, or 2), which can be controlled by stoichiometry (that is, the molar ratio of sulfuric acid in the IL, $\chi_{H_2SO_4}$), resulting in ILs with tuneable acidity. When sulfuric acid is used in excess to the base ($\chi_{H_2SO_4} > 0.5$), dimeric or oligomeric anions are formed, yielding ILs much more acidic than the corresponding equimolar mixtures ($\chi_{H_2SO_4} = 0.5$), on par with strong acids such as CF_3COOH or CF_3SO_3H. Hydrogensulfate ILs were found to be highly active acidic catalysts in a Fischer esterification.[25] Their economic feasibility was evaluated as very promising; the price of triethylammonium hydrogensulfate was estimated as US$1.24 kg^{-1}, similar to acetone or ethyl acetate.[26] Thus, hydrogen sulfate PILs appear to be candidates for large-scale acid-catalysed processes, with the potential to become a commercial reality.

In this work, we present a detailed analysis of the relationship between (i) the structure of anionic clusters, $[(HSO_4)(H_2SO_4)_x]^-$ ($x = 1$, or 2), in H_2SO_4-based PILs, (ii) their physicochemical properties, and (iii) their performance as acidic catalysts in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. This is proposed as a generic approach to tailoring ILs as a replacement for hazardous acids in industrially relevant reactions, generating both environmentally and economically sustainable processes.

Results and Discussion

Synthesis and Physicochemical Properties of ILs

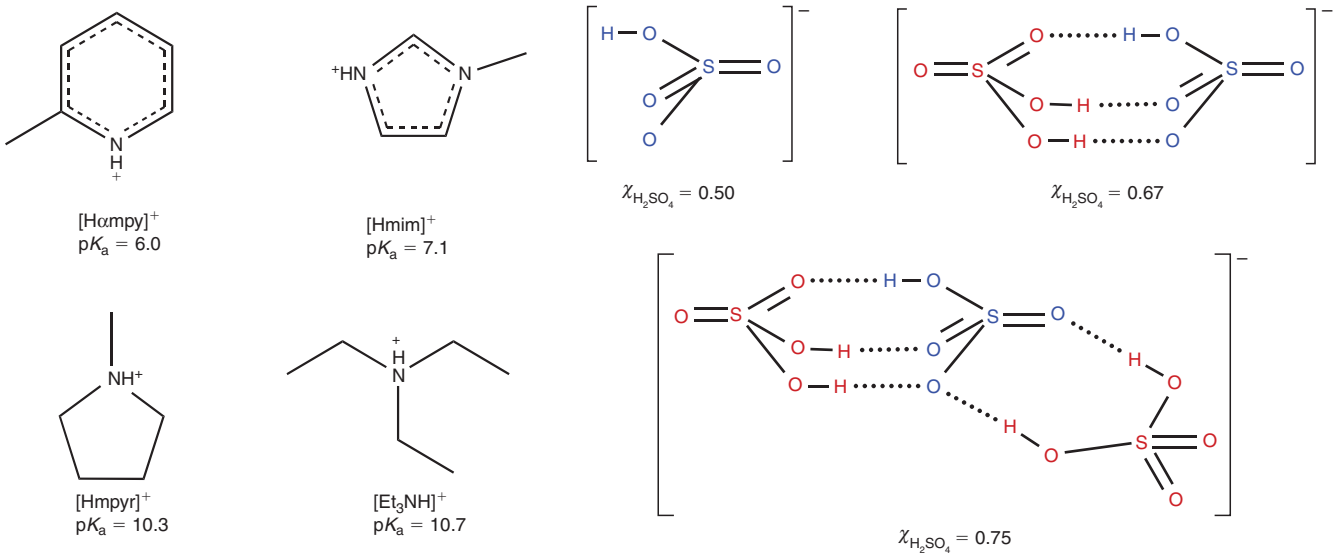
The PILs were prepared by the proton transfer reaction between sulfuric acid and amines, following the literature procedure.[25] The amines were selected to represent a variety of cation structures (aromatic, alicyclic, aliphatic), with a wide range of pK_a values (6.0–13.6), as shown in Scheme 2. The anion is of the general formula $[(HSO_4)(H_2SO_4)_x]^-$ ($x = 0$, 1, or 2), with its structure dependent on the molar ratio of sulfuric acid used for the synthesis, $\chi_{H_2SO_4}$ (Scheme 2). The structure of these liquids has been studied in detail previously,[25] and has been confirmed by ^{1}H NMR spectroscopy in this work.

The range of PILs presented here gives an opportunity to study the influence of both cation and anion structures on properties such as density, viscosity, conductivity, and catalytic activity in the Beckmann rearrangement. [Hαmpy][HSO_4] and [Et_3NH][HSO_4] are solids at room temperature, with melting points respectively of 64 and 75°C, therefore they were omitted during physicochemical characterisation.

Density

Densities (ρ) of the PILs were studied as a function of temperature and $\chi_{H_2}SO_4$ (Fig. 1). All ILs were denser than water, with both cation and anion influencing the density. The cation had the largest influence on the density of the IL series, following the general order: Et_3N (ρ_{Et3N} 0.726) < *N*-methylpyrrolidine (mpyr) (ρ_{mpyr} 0.819) < 2-picoline (αmpy) ($\rho_{\alpha mpy}$ 0.943) < 1-methylimidazole (mim) (ρ_{mim} 1.03 g mL^{-1}). An increase in the $\chi_{H_2}SO_4$ value also resulted in a measurable density increase: $\rho_{[Hmim][(HSO_4)(H_2SO_4)_2]} > \rho_{[Hmim][(HSO_4)(H_2SO_4)]} > \rho_{[Hmim][(HSO_4)]}$. It is worth noting that [Hmim][HSO_4] is characterised by a higher density than [Et_3NH][$(HSO_4)(H_2SO_4)_2$], possibly due to additional intermolecular interactions, such as π–π stacking and hydrogen bonding between imidazolium cations.

As expected, densities of all of the PILs decreased with increasing temperature; all data were fitted with a linear function



Scheme 2. Structures of cations and anions used in this work. pK_a values were measured in water.[27]

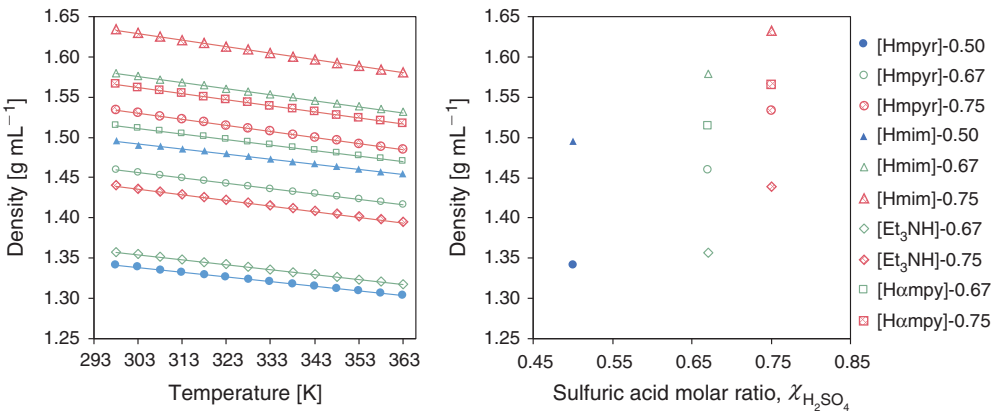


Fig. 1. Density of PILs based on sulfuric acid as a function of temperature (left) and the sulfuric acid content (right). Legend: [Hmpyr]-0.75 denotes [Hmpyr][$(HSO_4)(H_2SO_4)_x$], with $\chi_{H_2SO_4}$ 0.75.

(Eqn 1), where b is related to the expansion coefficient of the liquid.[28]

$$\rho = \alpha + bT \tag{1}$$

Fitting parameters reported in Table 1 indicate that, for each series based on the same proton cation, b values become more negative with increasing $\chi_{H_2SO_4}$; for example, for the [Hmim][$(HSO_4)(H_2SO_4)_x$] series, b decreases from $(-6.3 \pm 0.1) \times 10^{-4}$ g cm^{-3} K^{-1} for $\chi_{H_2SO_4}$ 0.50, to $(-8.21 \pm 0.03) \times 10^{-4}$ g cm^{-3} K^{-1} for $\chi_{H_2SO_4}$ 0.75. This suggests an increasing influence of temperature on density as the loading of sulfuric acid increases. This may reflect the increasing influence of more easily disrupted H-bonding in the liquid in contrast to the Coulombic interactions predominant at $\chi_{H_2SO_4} = 0.50$.

Table 1. Fitting parameters (Eqn 1) derived for density of PILs based on sulfuric acid

Cation	$\chi_{H_2SO_4}$	α [g cm^{-3}]	b ($\times 10^{-4}$) [g cm^{-3} K^{-1}]	R^2
[Hmpyr]	0.5	1.5146 ± 0.0008	-5.83 ± 0.02	0.9998
[Hmpyr]	0.67	1.6614 ± 0.0005	-6.76 ± 0.02	0.9999
[Hmpyr]	0.75	1.7598 ± 0.0009	-7.60 ± 0.03	0.9998
[Hmim]	0.50	1.681 ± 0.003	-6.3 ± 0.1	0.9973
[Hmim]	0.67	1.8014 ± 0.0009	-7.46 ± 0.03	0.9999
[Hmim]	0.75	1.8779 ± 0.0009	-8.21 ± 0.03	0.9999
[Et_3NH]	0.67	1.5404 ± 0.0005	-6.15 ± 0.02	0.9999
[Et_3NH]	0.75	1.6487 ± 0.0007	-7.02 ± 0.02	0.9999
[Hαmpy]	0.67	1.7200 ± 0.0007	-6.90 ± 0.02	0.9999
[Hαmpy]	0.75	1.7910 ± 0.0008	-7.58 ± 0.02	0.9999

Viscosity

Viscosities (η) of the PILs were studied as a function of temperature and $\chi_{H_2SO_4}$. Results are plotted as the Arrhenius plot and as viscosity as a function of the $\chi_{H_2SO_4}$ value (Fig. 2). Most notably, viscosities decrease dramatically with increasing molar ratio of sulfuric acid. This can be justified by the increasing dispersion of the anionic charge through cluster anions, [$(HSO_4)(H_2SO_4)_x$]$^-$ (Scheme 2). In addition, as

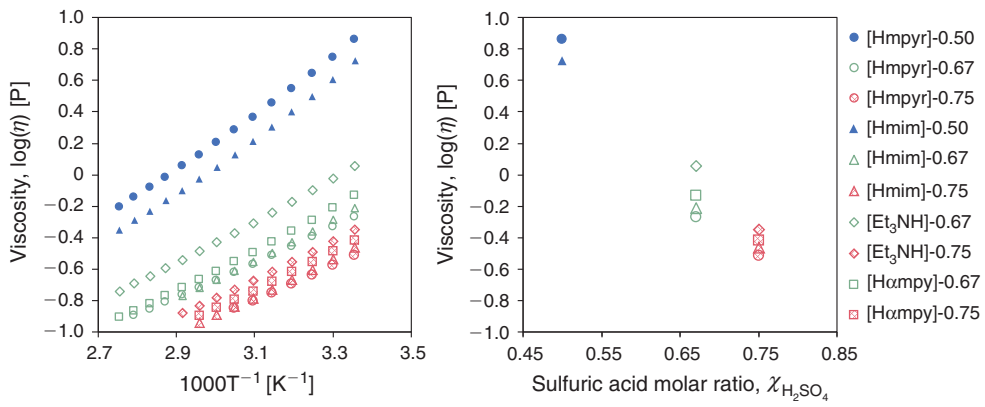


Fig. 2. Viscosity of PILs based on sulfuric acid: Arrhenius plot (left) and as a function of the sulfuric acid content (right). Legend: [Hmpyr]-0.75 denotes [Hmpyr][$(HSO_4)(H_2SO_4)_x$], with $\chi_{H_2SO_4}$ 0.75.

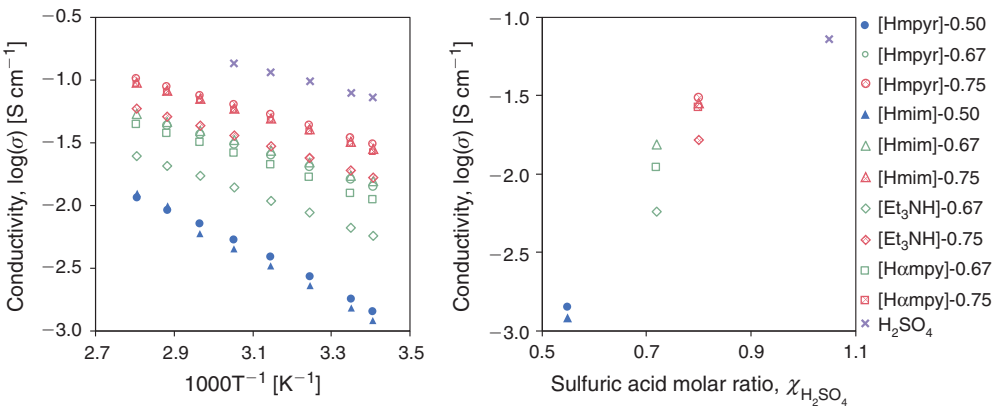


Fig. 3. Conductivity of PILs based on sulfuric acid: Arrhenius plot (left) and as a function of the sulfuric acid content (right). Legend: [Hmpyr]-0.75 denotes [Hmpyr][$(HSO_4)(H_2SO_4)_x$], with $\chi_{H_2SO_4}$ 0.75.

expected, viscosities decrease with temperature, and triethylammonium ILs are more viscous than the imidazolium and cyclic ammonium salts.

Conductivity

Conductivities (σ) of the PILs were studied as a function of temperature and $\chi_{H_2SO_4}$; corresponding plots are shown in Fig. 3.

Conductivity increased with the molar ratio of sulfuric acid, as expected from viscosity decreasing with $\chi_{H_2SO_4}$. The highest conductivity was recorded for concentrated sulfuric acid ($\chi_{H_2SO_4}$ 1.00), which derives from its viscosity being lower than that of ILs, and its ionicity being high due to autoprotolysis (intramolecular proton-switch mechanism, Eqn 2).[29]

$$2H_2SO_4 \rightleftharpoons [H_3SO_4]^+ + [HSO_4]^- \quad (2)$$

When a base is added to H_2SO_4, the resulting IL has anionic speciation dependent on the molar ratio of the acid. High concentrations of sulfuric acid ($\chi_{H_2SO_4} > 0.50$) produce protic, anionic clusters (Eqns 3 and 4), which may allow for an intramolecular proton-transfer mechanism enhancing conductivity, in addition to contributing to lower viscosity. Both of these contribute to conductivity being higher, although not as high as that of sulfuric acid. The $\chi_{H_2SO_4}$ 0.50 compositions contain a simple $[HSO_4]^-$ anion, which precludes autoprotolysis and contributes to high viscosity, resulting in low conductivities.

$$B + 3H_2SO_4 \rightarrow [HB]\left[(HSO_4)(H_2SO_4)_2\right] \quad \chi_{H_2SO_4}\ 0.75 \quad (3)$$

$$B + 2H_2SO_4 \rightarrow [HB][(HSO_4)(H_2SO_4)] \quad \chi_{H_2SO_4}\ 0.67 \quad (4)$$

$$B + H_2SO_4 \rightarrow [HB][HSO_4] \quad \chi_{H_2SO_4}\ 0.50 \quad (5)$$

Walden Plot

A traditional methodology of assessing the ionicity of ILs is based on the Walden plot approach (Fig. 4), where molar conductivity is plotted versus $(\text{viscosity})^{-1}$. The solid line is based on the conductivity of a dilute aqueous KCl solution, where both the anions and cations are able to move independently. ILs, for which the plots lie between '10 % ionisation' (dotted line in Fig. 4) and the ideal KCl line are considered to be 'good' ILs.[30] All of the studied PILs were found to lie in the 'good ILs' region of the Walden plot. However, no molar conductivities lying above the KCl line were noted, which would have been indicative of a proton hopping mechanism.

Molar conductivity data were fitted to the fractional Walden rule, Eqn 6, where the exponential component (γ) represents the slope in the plot of $\log\Lambda$ versus $\log(\eta^{-1})$, and assumes values

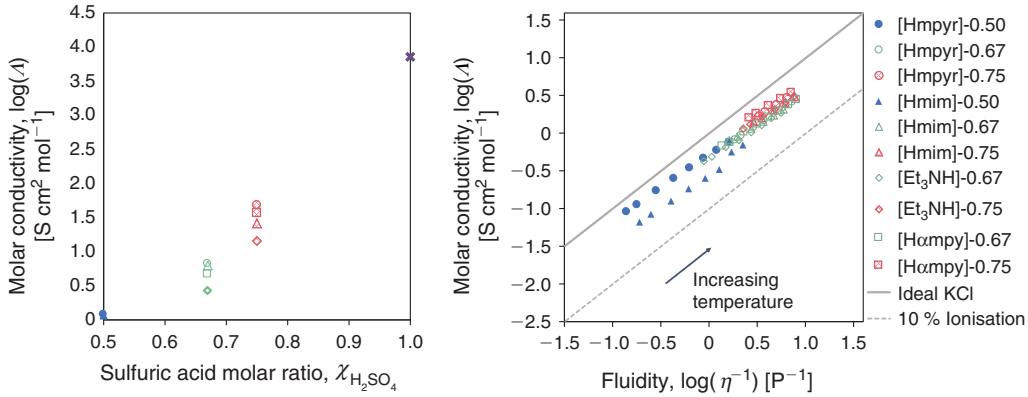


Fig. 4. Molar conductivity of PILs based on sulfuric acid as a function of the sulfuric acid content (left) and Walden plot (right). Legend: [Hmpyr]-0.75 denotes [Hmpyr][$(HSO_4)(H_2SO_4)_x$], with $\chi_{H_2SO_4}$ 0.75.

Table 2. Values of exponential component γ in Eqn 6, derived for the PILs based on sulfuric acid

Cation	$\chi_{H_2SO_4}$	γ
[Hmpyr]	0.50	0.866 ± 0.008
[Hmpyr]	0.67	0.844 ± 0.001
[Hmpyr]	0.75	0.833 ± 0.003
[Hmim]	0.50	0.94 ± 0.04
[Hmim]	0.67	0.739 ± 0.007
[Hmim]	0.75	0.766 ± 0.004
[Et_3NH]	0.67	0.808 ± 0.007
[Et_3NH]	0.75	0.793 ± 0.003
[Hαmpy]	0.67	0.794 ± 0.007
[Hαmpy]	0.75	0.789 ± 0.004

between zero and unity.[30,31] In physical terms, the γ value is related to the degree of decoupling of ion conduction modes of motions from the matrix modes that determine viscosity.[30]

$$\Lambda \cdot \eta^{\gamma} = \text{constant} \tag{6}$$

Exponential components from Eqn 6, calculated for the studied PILs based on sulfuric acid, vary between γ 0.739 and 0.944 (Table 2). The highest value was derived for [Hmim][$(HSO_4)(H_2SO_4)_x$], $\chi_{H_2SO_4}$ 0.50, γ 0.94 ± 0.04, which is near that of the KCl line and indicates high decoupling of ions. As a general trend, the γ value decreases slightly with increasing $\chi_{H_2SO_4}$, with the exception of the [Hmim][$(HSO_4)(H_2SO_4)_x$] series, where the lowest value is recorded for $\chi_{H_2SO_4}$ 0.67, γ 0.739 ± 0.007.

PILs Based on Sulfuric Acid as Catalysts for Beckmann Rearrangement

Brønsted acidic ILs act as both the solvent for the starting material (cyclohexanone oxime) and as the catalyst, enabling its rearrangement to the product. The product was observed to be readily separated by extraction in its neutral form and hence neutralisation of the product was not required. This is in contrast to experiments conducted in the presence of sulfuric acid in which after 10 min (110°C), a full conversion of oxime was achieved but to caprolactamium hydrogen sulfate. In the presence of the investigated ILs, generation of $(NH_4)_2SO_4$ as a by-product is entirely avoided. Since ILs are prepared in a one-step

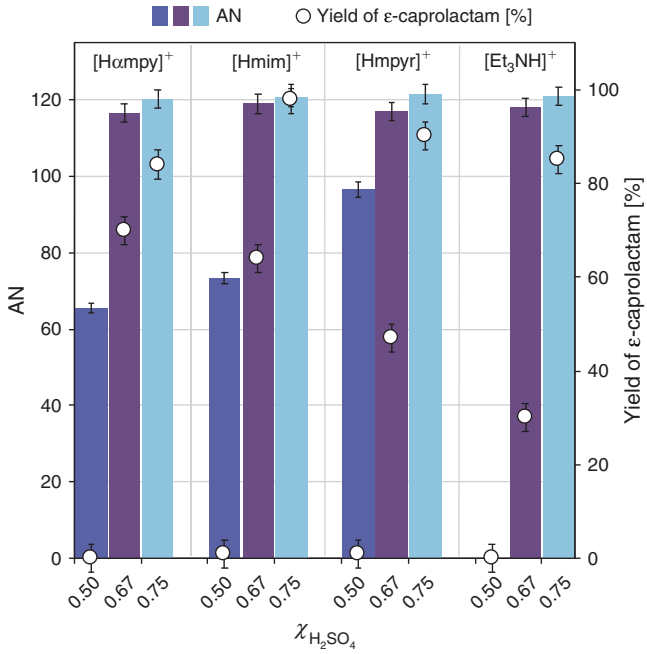


Fig. 5. Yield of ε-caprolactam in reactions catalysed with PILs based on sulfuric acid and four different bases, compared with AN values measured for these PILs. Yields were determined using HPLC. Reaction conditions: 110°C, 1000 rpm, molar ratio of PIL to cyclohexanone oxime 1.25 : 1; error bars represent standard deviation, $n = 3$.

acid–base neutralisation reaction, quaternisation with alkyl halides or with costly sultones is avoided. In conclusion, sulfuric acid-based PILs present themselves as industrially viable catalysts, which was the motivation to carry out this study.

Influence of PILs' Acidity

The Beckmann rearrangement was studied in the presence of twelve PILs, generated from four amines: 1-methylimidazole (mim), *N*,*N*,*N*-triethylamine (Et_3N), *N*-methylpyrrolidine (mpyr), and 2-picoline (αmpy), each combined with sulfuric acid at three different molar ratios ($\chi_{H_2SO_4}$ 0.50, 0.67, and 0.75). All PILs dissolved cyclohexanone oxime well, serving as both the reaction medium and the homogenous Brønsted acidic catalyst.

Fig. 5 provides comparison of the ε-caprolactam yields (circles) obtained using different PILs under the same reaction

conditions, and the acidity of each PIL, expressed as an acceptor number, AN (histogram bars).[25]

There is a certain correlation between the AN values determined for the PILs in our earlier work[25,32,33] and the yield of the ε-caprolactam. PILs with $\chi_{H_2SO_4}$ 0.50 are not catalytically active, which corresponds to their weak-to-medium acidity (AN 65.5–96.5). With $\chi_{H_2SO_4}$ 0.67, moderate to high yields of the product were obtained, in agreement with increasing AN. However, a broad distribution of conversions was observed for very similar AN values. Finally, all PILs at $\chi_{H_2SO_4}$ 0.75 composition produced high ε-caprolactam yields > 80 %, in agreement with the highest AN values reported for this group, but it is clear that an increase in catalytic performance between $\chi_{H_2SO_4}$ 0.67 and 0.75 is far more pronounced than would be expected from the small observed increases in AN values. As reported in our earlier work, for each acid catalyst under fixed reaction conditions, the relationship between AN values (representing a proton energy level) and conversion is described by a Boltzmann distribution, whereby at a certain acidity level there is a dramatic increase in conversion, and past this value, a further increase in AN brings no significant improvement.[32] Furthermore, it is clear here that the acid strength is not the only factor influencing the conversion, which is particularly pronounced at $\chi_{H_2SO_4}$ 0.67. Clearly, the nature of the cation plays a major role. The factor influencing the activity of the ILs is the pK_a value of the corresponding amines following the order: αmpy (6.0) < mim (7.1) < mpyr (10.3) < Et_3N (10.7) and indicating the strongest acidic character of αmpy. This behaviour is also followed at $\chi_{H_2SO_4}$ 0.75, except for [αmpy][$(HSO_4)(H_2SO_4)_2$], where we speculate that diffusion could impair kinetics.

The highest activity was reported for the [Hmim][$(HSO_4)(H_2SO_4)_2$] system, which gave full conversion of cyclohexanone oxime within 15 min. This IL was chosen for further study under varying reaction conditions.

Influence of Catalyst Loading and Reaction Conditions

Considering that the IL was used as both the catalyst and the solvent, it was necessary to determine its amount to provide sufficient catalytic activity, but also to enable mass transport. The reaction has been studied as a function of the [Hmim][$(HSO_4)(H_2SO_4)_2$] loading (0.50 to 1.50 in PIL to oxime mol ratio), with results reported in Table 3. Full conversion of cyclohexanone oxime was achieved within 15 min when using either a 1.5 or 1.25 PIL-to-oxime mol ratio, whereas lower PIL loading impaired the dissolution of the starting material, decreasing the reaction rate. Therefore, a 1.25 PIL-to-oxime ratio was used for further studies.

The influence of reaction temperature and time was studied across the temperature range of 80 to 130°C (Fig. 6). At the two highest studied reaction temperatures, 120 and 130°C, conversion of cyclohexanone oxime was completed within 10 min; however, the reaction mixture darkened, most probably due to side reactions. Although all investigated PILs have good thermal stability (T_d > 200°C),[25] the Beckmann rearrangement is a highly exothermic reaction (1815 kJ kg^{-1}),[2] and exceeding the process temperature of 120°C resulted in thermal runaway above 200°C, inducing cyclohexanone oxime thermal degradation. At reaction temperatures of 100°C and lower, the reaction rate decreased significantly, without reaching full conversion of oxime within an hour. As a consequence, the initially selected reaction temperature of 110°C was found to be optimal.

Table 3. The influence of the [Hmim][$(HSO_4)(H_2SO_4)_2$]-to-oxime ratio on the ε-caprolactam yield

Reaction conditions: 110°C, reaction time 15 min, 1000 rpm. Uncertainties represent standard deviation, $n = 3$

PIL-to-oxime mol ratio	Yield ± 3 [%]
0.00	0
0.50	37
0.75	70
1.00	85
1.25	100
1.50	100

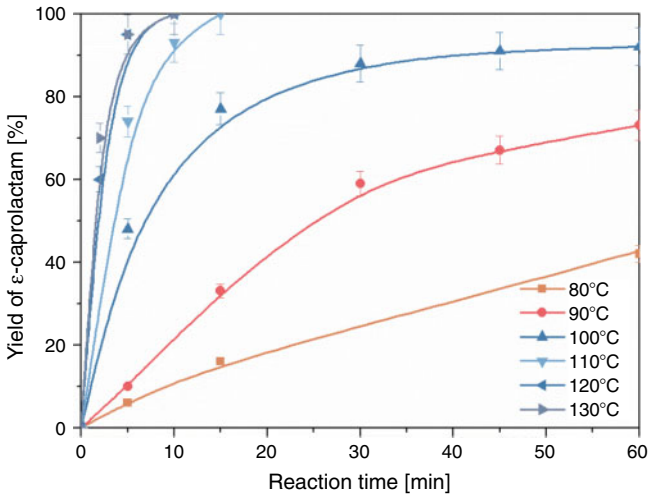


Fig. 6. Yield of caprolactam as a function of reaction time, at a range of reaction temperatures. Reaction conditions: molar ratio of [Hmim][$(HSO_4)(H_2SO_4)_2$] to cyclohexanone oxime 1.25:1; 1000 rpm; error bars represent standard deviation, $n = 3$.

Recycling study

Recycling was studied under optimised reaction conditions: 110°C, 20 min, 1.25 mol ratio of [Hmim][$(HSO_4)(H_2SO_4)_2$] to oxime. Following the reaction, extraction of the product from the neat IL phase was impossible due to its high viscosity, but this was addressed by the addition of deionised water. From the aqueous solution, complete product extraction was achieved with CH_2Cl_2. Subsequently, the IL phase was dried using a rotary evaporator, then a Schlenk line (high vacuum), and reused in the next reaction. Compared with the very high conversion (100 %) and selectivity (99 %) in the first reaction cycle, recycled PIL saw a significant drop in both conversion (70–79 %) and selectivity (76–78 %) in the second and third reaction cycles. Furthermore, in the 4th reaction cycle conversion (31 %) and selectivity (40 %) decreased further.

Comparing the ^{1}H NMR spectra of products isolated from the first and second reaction cycles (Fig. 7), the spectrum of the latter featured a new peak at δ 10.08, assigned to the acidic proton from caprolactamium hydrogen sulfate, which is known to form in conventional sulfuric acid or oleum-catalysed Beckmann rearrangement (Scheme 3).[3] Since it has not been observed in reactions with fresh ILs, it was concluded that caprolactamium hydrogen sulfate formed as a side-product to ε-caprolactam, as a consequence of water addition to the IL phase during extraction. It is plausible that water interacted with

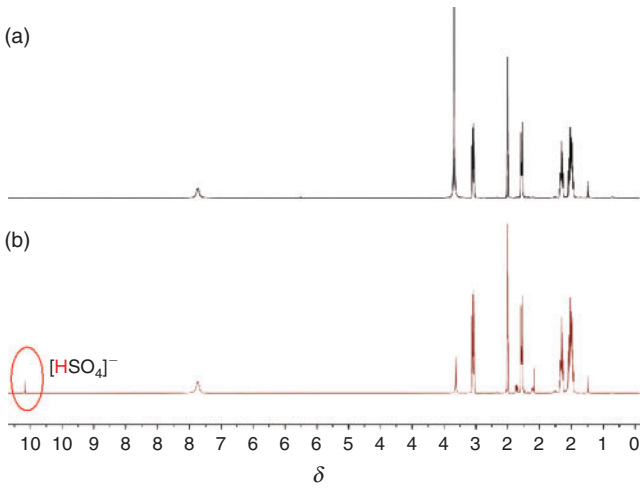


Fig. 7. ^{1}H NMR spectra of the ε-caprolactam in DMSO after (a) first and (b) second reaction cycle.

Scheme 3. Protonation of ε-caprolactam to give caprolactamium hydrogen sulfate.[3]

the $[(HSO_4)(H_2SO_4)_2]^-$ anion to abstract a proton and form $[H_3O]^+$, releasing more $[HSO_4]^-$. Despite drying the PIL under high vacuum (24 h, 70°C) before each reaction cycle, water bound in the form of a hydronium cation might have remained in the IL structure, and the equilibrium was not reversed towards $[(HSO_4)(H_2SO_4)_2]^-$. Moreover, the formation of caprolactamium hydrogen sulfate consumes the excess acid, driving activity down in the following cycles.

In conclusion from the recycling experiments, whereas work presented in this contribution focussed on characterisation of the catalyst and screening of the reaction conditions, its continuation should focus on optimisation of the extraction step. A polar aprotic solvent may be considered to replace water as a diluent of the IL layer, altering the cation to decrease viscosity, or an efficient engineering solution may be adopted to overcome the viscosity issue. In addition, alternatives to CH_2Cl_2 may be considered, to better conform to sustainable solvent selection rules.

Comparison of the Optimised System with the Literature

The literature studies using IL-based catalytic systems to synthesise ε-caprolactam are compared with this work in Table 4. The approach presented in this work offers the shortest reaction time by far to achieve full conversion (15 min); albeit the reaction temperature is higher than in most literature reactions, it is still moderate. Using PILs, no additional acidic catalyst or solvent is required. Finally, the simplicity of the one-step, solventless synthesis of PILs affords an inexpensive and sustainably generated catalyst, containing no halogen atoms. The only shortfall of the system presented here is the extraction step, which needs to be optimised as discussed above in order to deliver an industrially viable catalyst for clean ε-caprolactam synthesis.

Experimental

Materials

1-methylimidazole (≥ 99 %, purified by redistillation), triethylamine, 2-picoline, *N*-methylpyrrolidine, cyclohexanone oxime, and sulfuric acid were purchased from Sigma–Aldrich and used as received.

Synthesis

PILs

All PILs were prepared according to general procedure, on a 10 g scale. 1 mol equiv. of amine was weighed into a round-bottom flask, equipped with a stirring bar and placed in an ice bath. The required amount of sulfuric acid (1, 2, or 3 mol equiv.) was added dropwise to the stirred amine, and then the mixture was stirred for another 1 h at 50°C to ensure complete proton transfer. Subsequently, the ILs were dried under high vacuum (50°C, 10^{-2} bar, overnight). ILs were obtained with a high yield in a range between 97 and 99 %. The structures of the studied cations and anions are presented in Scheme 2.

Beckmann Rearrangement

All reactions were carried out under dry nitrogen in a one neck round bottom flask, on a 0.1 g scale according to the cyclohexanone oxime. Starting material and IL in proper molar ratio (0, 0.5, 0.75, 1.00, 1.25, 1.50) were weighed into a flask. Subsequently the mixture was placed in an oil bath at the desired temperature (80–130°C) and vigorously stirred (1000 rpm). The reaction was carried out for 5–60 min, afterwards the mixture was homogenised with water and the ε-caprolactam yield was monitored by HPLC. All experiments and HPLC analysis were performed in triplicate. The isolation of the product was conducted for the scaled up experiment (×10) by addition of water (10 mL) followed by extraction with CH_2Cl_2 (4 × 25 mL) affording 0.86 g of product (yield 86 %). δ_H (400 MHz, DMSO) 7.37 (s, 1H), 3.04 (dd, *J* 10.0, 5.9, 2H), 2.30–2.27 (m, 2H), 1.93–1.57 (m, 2H), 1.54–1.37 (m, 4H).

Recycling of IL

In a typical experiment where the IL was recycled, reactions were scaled up by a factor of ten. A mixture of cyclohexanone oxime (10.0 mol) and IL (12 mol-%) were stirred for 20 min at 110°C. The mixture was cooled to room temperature, water (10 mL) was added, and the product was extracted with CH_2Cl_2 (4 × 25 mL). The water was removed from the IL phase by rotary evaporator, and the IL was further dried under vacuum (70°C, 10^{-2} bar, 6 h) and reused in the next reaction.

Characterisation

HPLC analysis was performed using a Waters 2996 chromatograph equipped with a Symmetry C18 5.0 μm (2.1 mm × 150 mm) column and photodiode array detector. The ^{1}H NMR spectra were recorded at 400 MHz and the ^{13}C spectra were recorded at 100 MHz (Agilent spectrometer), δ values are in parts per million (ppm) relative to tetramethylsilane (TMS) as an internal standard.

Density

The densities were measured using an Anton Paar DMA 5000 density meter precise to ± 0.0005°C and ± 0.00001 g cm^{-3} (uncertainties obtained from three independent measurements) in the temperature range between 25 and 90°C.

Table 4. Comparison of the performance of IL-based catalytic systems for Beckmann rearrangement, described in the literature and in this work

Catalyst & solvent	Conversion [%]	Selectivity [%]	Reaction conditions	Catalyst-to-substrate molar ratio	IL-to-reaction mixture molar ratio	Ref.
$[Hmim][(HSO_4)(H_2SO_4)_2]_2$	100	99	15 min, 110°C	1.25 : 1	0.556	This work
Eaton's reagent & $[bmim][PF_6]$	—	99	21 h, 75°C	0.1 : 1	0.688	[6]
Metaboric acid & $[bmim][PF_6]$	98	> 99	3 h, 90°C	3 : 1	0.548	[7]
1-(3-Chlorosulfonylpropyl)-3-ethylimidazolium hexafluorophosphate	99	98	2 h, 80°C	1 : 1	0.500	[12]
Tosyl chloride & [Hmim][TFA]	100	99	2,5 h, 50°C	1.1 : 1	0.846	[13]
1-Methyl-3-(butyl-4-sulfonyl)imidazolium hydrogen sulfate	> 99	> 99	4 h, 80°C	5 : 1	0.832	[19]
N,*N*′-di(3-sulfopropyl) 4,4′-dipyridinium phosphotungstate benzonitrile	100	73	2 h, 130°C	0.1 : 1	0.002	[17]

Viscosity

The viscosities were determined using an Anton Paar microviscometer (Lovis 2000 M) which uses a falling ball technique, over a temperature range of 25 and 90°C, with standard deviation across the three measurements for each experiment being less than 0.005 *P* (uncertainties obtained from three independent measurements). For the measurement, a gold ball was used to avoid corrosion.

Conductivity

Electronic impedance spectroscopy (EIS) was used to determine ionic conductivity of the ILs by measuring their resistance and impedance as a function of frequency ranging from 0.1 Hz to 10 MHz. Measurements were performed using a Solartron 1296 dielectric interface linked to a 1290 frequency response analyser in a temperature range of 25 to 90°C, with standard deviation across the three measurements for each experiment being less than 0.0002 S cm^{-1} (uncertainties obtained from three independent measurements). Obtained data were analysed using Solartron impedance measurement software (version 3.3.1). A two-electrode platinum wire dip cell was used, with the cell constant determined using 0.01 M KCl(aq) solution.

Conclusions

Conventional, widely used ε-caprolactam production through the Beckmann rearrangement of cyclohexane oxime is catalysed by oleum, and proceeds through the formation of caprolactamium hydrogen sulfate, which needs to be neutralised with ammonia to isolate the product. This generates $(NH_4)_2SO_4$ as a by-product; although it is used as a fertilizer, the amount produced every year exceeds demand in that market. Furthermore, its separation decreases the yield of isolable ε-caprolactam. This work offers the promise of a sustainable and economically competitive process, whereby the neutralisation step is avoided by the use of a highly Brønsted-acidic, PIL based on sulfuric acid in a dual role of solvent and catalyst.

PILs were prepared by the reaction between sulfuric acid and tertiary/aromatic amines. Their acidity was controlled by the amount of sulfuric acid component in the IL. When used in excess, sulfuric acid forms oligomeric, hydrogen-bonded anionic complexes; altering the content of sulfuric acid allows tuning not only of acidity, but also other properties including viscosity, density, and conductivity.

A very high catalytic activity of the sulfuric acid-based PILs in the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam was recorded, leading to full conversions and very high selectivities (110°C, 15 min). Product could be isolated by simple extraction, without the requirement for the neutralisation step. Recycling experiments suggest that the extraction step requires further optimisation, to avoid using water as viscosity modifying additive, which was found detrimental to the longevity of the catalyst.

Conflicts of Interest

The authors declare no conflicts of interest.

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