Ammonia capture from the gas phase by encapsulated ionic liquids (ENILs)†

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Encapsulated ionic liquids (ENILs) based on carbonaceous submicrocapsules were designed, synthesized and applied to the sorption of NH₃ from gas streams. The ENILs were prepared using three different task-specific ILs with adequate properties for NH₃ capture: 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (EtOHzimBF₄), choline bis(trifluoromethylsulfonyl)imide (CholineNTf₂) and tris(2-hydroxyethyl)methylammonium methylsulfate [(EtOH)₃MeNMeSO₄]. The ENILs synthesized were analyzed by different techniques to assess their morphology, chemical composition, porous structure and thermal stability. The capture of NH₃ was tested in fixed-bed experiments under atmospheric pressure. The influence of the type and load of IL, temperature (30, 45 and 60 °C) and NH₃ inlet concentration was analyzed. Desorption of NH₃ from the exhausted ENILs was also studied at atmospheric pressure and temperatures in the range of 150 to 200 °C. The ENILs prepared with task-specific ILs were found to be suitable for NH₃ capture in the fixed-bed operation. These systems can be a promising alternative to conventional absorption or adsorption due to: (i) high sorption capacity controlled by IL selection, (ii) remarkable mass transfer rate, (iii) low sensitiveness to high temperatures of the gas stream, (iv) fast and complete regeneration of the exhausted ENIL at mild conditions; and (v) recovery of NH₃.

1. Introduction

Ammonia is present in gas streams from a diversity of industries and processes, including food processing, compost plants, fishery operations, rubber and leather manufacture, livestock crematoria, and wastewater treatment plants, among others. NH₃ emissions contribute significantly to fine particulate matter formation, eutrophication of ecosystems, acidification of soils, alteration of the global greenhouse balance and odor problems. Different approaches have been proposed to remove NH₃ from gas effluents. Dry adsorbents, such as activated carbon (AC), have attracted much attention due to their simple design and operation. On the other hand, in the past years ionic liquids (ILs) have generated interest for the development of a large array of engineering applications, including their use as absorbents in gas separation processes. The studies available reveal the great potential of ILs to absorb NH₃. It has been demonstrated that the cation and anion can be successfully selected to improve both the thermodynamics and kinetics of NH₃ absorption. In fact, recent works have evaluated the excellent performance of ILs as NH₃ absorbents in industrial processes of interest, such as absorption refrigeration cycles. However, the transport properties of ILs represent still a main limitation for practical applications, in particular, ILs generally exhibit much higher viscosity than conventional organic solvents.

In this sense, novel materials named Supported Ionic Liquid Phase (SILP), consisting of the immobilization of ILs on a solid support, have been proposed as a technical solution to overcome the mass transfer limitations of ILs in gas–liquid separation processes. SILP materials are commonly prepared by spreading a thin layer of IL onto the surface of a solid support, mostly consisting of materials with high specific surface area, like TiO₂, SiO₂ or AC. It has been demonstrated that the IL immobilization on a porous support drastically increases the gas/liquid contact area, leading to much faster sorption rates than in the case of bulk IL. However, one of the main drawbacks for the application of SILP materials in gas separation processes is the limited amount of IL uploaded onto the support (generally lower than 20% w/w, reaching up to 50% w/w in some cases), that limits their application in gas separation processes. In this context, the new concept of encapsulated ionic liquids (ENILs) has arisen as an interesting alternative. In a pioneer work, Deng et al. synthesized a highly dispersed IL material through the physical encapsulation of the IL in a silica-gel matrix through a sol–gel process, thus reaching IL contents from 8 to 53% w/w.
Nanocomposites of ILs confined in mesoporous silica gels were successfully applied to the selective adsorption of CO2/N2 streams.48 We recently presented ENIL materials53 consisting of hollow carbonaceous submicrocapsules (Ccap) that confine ILs.54–56 The synthesis of ENILs is favored by the high affinity found between ILs and AC.56–59 The novel material is characterized by a high amount of IL incorporated (70–85%, w) and capsule particle size ranging from 450 to 800 nm. This ENIL material implies a shift from a continuous to a discrete IL phase with submicron size units, thus drastically increasing the specific contact area with respect to the neat IL.56 Moreover, ENIL show the additional advantage of their high versatility, since they can be prepared at different loads (up to 80% w/w) using ILs with optimized properties for a specific application. In a previous work,53 the capture of NH3 was preliminary tested at atmospheric pressure with ENILs prepared using the task-specific IL 1-2-(hydroxyethyl)-3-methylimidazolium tetrafluoroborate (EtOHmimBF4), choline bis(trifluoromethylsulfonyl)imide (CholineNTf2) and tris(2-hydroxyethyl)-methylammoniummethylsulfate [[EtOH]3MeNMeSO4] (Table 1). The ENILs were characterized by several techniques, including scanning and transmission electron microscopy (SEM and TEM), elemental analysis (EA), N2 adsorption–desorption at −196 °C and thermogravimetric analysis (TGA). They were compared to the corresponding benchmark materials namely the empty carbon submicrocapsules (Ccap) and the neat ILs. The fixed-bed sorption experiments were carried out in fixed bed at temperatures ranging from 30 to 60 °C and inlet NH3 concentrations from 500 to 2000 ppmv. The influence of the chemical nature and the load of IL in the ENILs was analyzed at different operating conditions. The regeneration of the exhausted ENIL beds was assessed by desorption experiment performed under N2 flow at temperatures between 120 and 200 °C.

2. Materials and methods

2.1. Materials

Phenol (99%), paraformaldehyde (95–100%), aluminum trichloride (95–100%), ammonia (38%), absolute ethanol, hydrofluoric acid (48%) and sodium hydroxide was purchased from

Table 1  Ionic liquid structures and abbreviations

| Structure | Abbreviation | Name |
|-----------|--------------|------|
|          | EtOHmimBF4   | 1-(2-Hydroxyethyl)-3-methylimidazolium tetrafluoroborate |
|          | CholineNTf2  | Choline bis(trifluoromethylsulfonyl)imide |
|          | (EtOH)3MeNMeSO4 | Tris(2-hydroxyethyl)methylammonium methylsulfate |
Panrec, and tetraethylorthosilicate (98%) (TEOS) and octadecyltrimethoxysilane (90%) (C18TMS) from Sigma-Aldrich. The ILs 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate (EtOHmimBF4), choline bis( trifluoromethylsulfonyl) imide (CholineNTf2), and tris[2-hydroxyethyl]-methylammonium methylsulfate [(EtOH)3MeNMeSO4] were supplied by Iolitec in the highest purity available (purity > 97–98%). They were used as received.

To prevent hydration, acetone and ILs were kept in their original tightly closed bottles in a desiccator before use, and they were manipulated inside a glovebox under dry nitrogen atmosphere.

The sorption experiments were carried out using a commercial mixture of N2 and NH3 (2000 ppmv) and N2 (purity > 99.99%) supplied by Praxair.

2.2. Preparation of ENILs
Carbon submicrocapsules (Ccap) with a thick wall were synthesized following the template method, as detailed in previous works,\(^{33,36}\) to achieve high mechanical resistance and porosity. The Ccap were filled by successive impregnation steps of 100 mg of hollow carbon capsules with 1 mL of IL–acetone solution.\(^{36}\) The number of impregnation steps and the concentration of IL in the acetone solution were adjusted to obtain ENILs with different IL loadings. To ensure a homogeneous penetration of the IL solution into the pores, it was added dropwise over the Ccap followed by vacuum evacuation of acetone at 60 °C and 10 mbar for 2 h. The ENILs synthesized contained from 33 to 80% of IL (w, ENIL basis), i.e. IL/carbon mass ratios between 0.5 and 4 (R0.5–R4). The amount of IL loaded was calculated as the difference between the weight of the final ENIL and the starting Ccap. Those measurements were validated by the N content determined by elemental analysis (EA), as established in a previous work.\(^{36}\)

All the ENILs prepared had the resemblance and texture of a powdered material. The ENILs were stored at 90 °C during 24 h prior to their use.

2.3. Characterization of ENILs
The morphology and microstructure of Ccap and ENILs were studied by scanning and transmission electron microscopy (SEM and TEM). SEM micrographs were obtained using a Hitachi S-3000N model and TEM images in a Philips 420 microscope. Elemental analyses (EA) of Ccap and ENILs were carried out in a Perkin-Elmer analyzer (210 CHN model) to obtain C, H and N content. The porous structure was characterized by means of nitrogen adsorption–desorption isotherms at -196 °C using a Micromeritics apparatus (Tristar II 3020 model). The samples were previously outgassed at 150 °C and 70 mTorr for 6 h. The BET equation was applied to determine the total surface area (A\(_{\text{BET}}\)), and the external or non-micropore area (A\(_{e}\)) was obtained using the t-method. The Dubinin–Radushkevich equation was applied for micropore volume estimation. The difference between the volume of N\(_2\) adsorbed (as liquid) at 0.95 relative pressure and the micropore volume was taken as the mesopore volume, and the DFT method was used to obtain the pore size distribution.\(^{34}\) Thermogravimetric analyses (TGA) of ILs and ENILs were conducted in a Mettler Toledo Instrument (TGA/SDTA851e model) under nitrogen atmosphere. A dynamic method was used within the temperature range from 50 to 600 °C at a heating rate of 10 °C min\(^{-1}\) under a nitrogen flow of 50 mL min\(^{-1}\). The accuracy of temperature and mass measurements was 0.1 °C and 10\(^{-3}\) mg, respectively. Aluminum pans were used to hold an initial mass between 4 and 12 mg. The derivative curves (DTG) were also obtained to assess the temperature of IL decomposition in the ENILs.

2.4. NH\(_3\) capture experiments
The sorption of ammonia was performed in a fixed bed with the ENIL (50–250 mg) placed in a quartz column (4 mm of internal diameter and 4–5 cm of length). N\(_2\)–NH\(_3\) mixtures (500–2000 ppmv NH\(_3\)) were continuously passed at 20 mL min\(^{-1}\) flow rate. Different temperatures within the 30–60 °C range were tested and the operating pressure was \approx \text{atm}. NH\(_3\) was analyzed at the exit of the column with a quadrupole mass analyzer (Omnistar/ThermoStar).

The NH\(_3\) uptake at saturation (\(q_\text{v}, \text{mg g}^{-1}\)) for Ccap and ENILs were calculated from the breakthrough curves as:

\[
q_v = \frac{Q}{m} \int_{t_o}^{t_f} (C_o - C) \, dt
\]

where Q is the gas flow rate (L min\(^{-1}\)); m is the mass of Ccap or ENIL in the column (g); C and \(C_o\) represent the exit and the inlet NH\(_3\) concentration (mg L\(^{-1}\)), respectively, and \(t_o\) corresponds to the time at which \(C = C_o\). The comparison of the capacity of the different ENILs was made in terms of per unit mass of ENIL (\(q_\text{v,ENIL} \text{, mg g}^{-1}\text{ENIL}^{-1}\)), unit mass of IL (\(q_{\text{u,IL}} \text{, mg g}^{-1}\text{IL}^{-1}\)) or unit volume of the packed bed (\(q_{\text{v,ENIL}} \text{, mg cm}^{-3}\)). The breakthrough time (\(t_o\)) was defined as the time at which the C/C\(_{o}\) ratio reached a value of 0.05.

The length of the mass transfer zone (\(h_{\text{MTZ}}\)) was estimated from the breakthrough curves using the expression:

\[
h_{\text{MTZ}} = \frac{(t_{o.95} - t_{0.95})}{t_{0.95}} h
\]

where \(h\) is the length of the entire sorbent bed in the columns, \(t_{o.95}\) and \(t_{0.05}\) are the times at which the exit NH\(_3\) concentration reaches 95% and 5% of the inlet value, respectively.

Desorption experiments were performed after the saturation of the ENIL beds. A N\(_2\) flow (1 mL min\(^{-1}\)) was passed through the exhausted bed at 200 °C during 30 minutes. In the case of (EtOH)\(_3\)MeNMeSO\(_4\), a regeneration temperature of 150 °C was used because of the lower thermal stability of this IL. The ENIL fixed beds were used in three sorption–desorption cycle tests.

3. Results and discussion
3.1. Preparation and characterization of ENILs
The selection of ILs for this work (EtOHmimBF4, CholineNTf2 and (EtOH)\(_3\)MeNMeSO\(_4\)) was conducted taking into consideration that ILs with acidic character and low Henry constants of NH\(_3\) can lead to ENILs with high capacity for NH\(_3\) capture. Previous works indicated that the inclusion of hydrogen-bond donor groups, such
as hydroxyl group, in the IL structure significantly increases the interaction with NH₃, and thus its solubility.²²,²³ Table 2 collects the most relevant physical and thermodynamic properties of the task-specific ILs used in this work.

A set of ENILs based on EtOHmimBF₄ and different IL loads (R₀,5, R₁, R₂, and R₄) were prepared with the view in analyzing their properties and behavior in NH₃ capture. Additional ENILs incorporating a high load (R₂) of CholineNTf₂ and (EtOH)₃MeNMeSO₄ were also prepared in order to also check the influence of the nature of the IL.

The SEM image of C_cap (Fig. 1A) showed regular spherical morphology and a mean diameter around 600 nm. A wall thickness ca. 80 nm can be measured from TEM image (Fig. 1B). The TEM image (Fig. 1C) of the ENIL–R₄ prepared with EtOHmimBF₄ shows successful incorporation of the IL into the C_cap structure, both in the hollow core and in the porous carbon wall. The EA results in Table 3 also confirm the adequate incorporation of IL into the ENILs.

Adsorption–desorption isotherms of N₂ at −196 °C were used to analyze the porous structure of C_cap and ENILs, being the results collected in Table 3. C_cap showed a highly developed porous structure (A_BET = 1503 m² g⁻¹), with high contributions of micro- and mesoporosity, as indicated by the high amount of nitrogen adsorbed in the whole relative pressure range. Fig. 2A shows the isotherms obtained for ENILs with different loads of EtOHmimBF₄. The porosity available for nitrogen adsorption decreases clearly as the load of IL increases. In fact, for ENIL–R₀.5 (33% of IL) a reduction of 65% in the BET surface area takes place (Table 3), whereas for ENIL–R₁ (50% of IL) only 13% of the initial BET surface area of the C_cap is still available for N₂ adsorption. The BET surface area decreases to negligible values for R₂, and particularly for R₄ (80% of IL). Fig. 2B shows that the loss of porosity takes place evenly in the whole range of porosity with the increase in the load of IL. Table 3 also summarizes the characteristics of the ENILs prepared with CholineNTf₂ and

| Material | ENIL nominal IL load (% w/w) | %C | %H | %N | ENIL calculated IL load (% w/w) | A_BET (m² g⁻¹) | Aₚ (m² g⁻¹) | V_microp (cm³ g⁻¹) | V_mesp (cm³ g⁻¹) | Thermal stability, T_DTG (°C) |
|----------|-------------------------------|----|----|----|-------------------------------|----------------|--------------|-----------------|-----------------|-----------------|
| C_cap    | —                             | 88.2 | 1.0 | 0.2 | —                             | 1503           | 701          | 0.32            | 0.53            | —               |
| ENIL–R₀.₅ | EtOHmimBF₄                   | 33  | 70.0 | 2.7 | 4.3                          | 519            | 297          | 0.19            | 0.22            | —               |
| ENIL–R₁   |                              | 50  | 60.1 | 3.4 | 6.9                          | 197            | 108          | 0.06            | 0.08            | 385             |
| ENIL–R₂   |                              | 67  | 52.9 | 3.8 | 8.7                          | 13             | 12           | 0.00            | 0.01            | 397             |
| ENIL–R₄   |                              | 80  | 46.3 | 4.4 | 10.5                         | 1              | 1            | 0.00            | 0.00            | 405             |
| ENIL–R₄   | CholineNTf₂                   | 80  | 36.1 | 3.1 | 5.8                          | 2              | 2            | 0.00            | 0.00            | 392             |
| ENIL–R₄   | (EtOH)₃MeNMeSO₄              | 80  | 48.4 | 5.6 | 4.4                          | 3              | 3            | 0.00            | 0.00            | 242/318         |
| ENIL–R₄   | EtOHmimBF₄                   | —   | -   | -   | -                            | -              | -            | -              | -               | -               |
| ENIL–R₄   | CholineNTf₂                   | —   | -   | -   | -                            | -              | -            | -              | -               | -               |
| ENIL–R₄   | (EtOH)₃MeNMeSO₄              | —   | -   | -   | -                            | -              | -            | -              | -               | -               |

Table 2 Physical and thermodynamic properties of the IL studied²²,²³

Table 3 Characterization of the C_cap and ENILs prepared with different load of IL
(EtOH)₃MeNMeSO₄, showing also nearly total loss of porosity ($A_{BET} < 3 \text{ m}^2 \text{ g}^{-1}$) for $R_4$ independently of the IL used.

Thermal stability is also an important factor to be considered for the application of ENILs. Fig. 3A depicts the TGA curves of the neat IL EtOHmimBF₄ and $C_{cap}$. As can be seen, EtOHmimBF₄ starts to decompose around 340 °C and it is decomposed almost completely at 460 °C. $C_{cap}$ exhibits a loss of weight lower than 10% in the temperature range considered, which can be ascribed to the gradual loss of surface chemical groups. The thermal stability of the ENILs prepared with EtOHmimBF₄ can be compared with that of the neat IL in Fig. 3B (see also Fig. 1S in ESI† for complete TGA data). Previous studies⁴⁶,⁶² showed that the thermal stability of supported ILs can be remarkably affected by the nature of the support, with non-polar porous surfaces, such as activated carbon, leading more stable SILP than supports with acidic character, such as silica. Fig. 3B and Table 3 (see $T_{DTG}$ values) show that the thermal stability of ENIL materials is slightly lower than that of the neat IL, in agreement with the low support effect observed with carbon surfaces containing low concentration of polar functional groups,⁴⁶ which is the case of $C_{cap}$. In addition, it can be observed that an increase of the IL load results in higher thermal stability of the ENIL material, with a shift in the DTG degradation peak ($T_{DTG}$) from 385 to 405 °C. This shift is probably related to the decreasing proportion of IL in contact with the support surface. Thus, ENIL–$R_4$ presents a thermal stability very close to that of the neat IL EtOHmimBF₄. Table 3 also summarizes the $T_{DTG}$ for the ENIL–$R_4$ prepared with CholineNTf₂ and (EtOH)₃MeNMeSO₄ (complete TGA curves in Fig. 2S and 3S in ESI†). It can be concluded that ENILs, particularly $R_4$, present an adequate thermal stability to operate in the 30–200 °C range of sorption/desorption temperatures involved in the NH₃ capture and bed regeneration processes.

3.2. Capture experiments in fixed-bed column

Fig. 4 depicts the NH₃ breakthrough curves obtained using a packed bed of $C_{cap}$ at temperatures of 30, 45 and 60 °C. Table 4

![Fig. 2](image2.png)  (A) Nitrogen adsorption–desorption isotherms at −196 °C and (B) pore size distribution (1 to 100 nm) of $C_{cap}$ and ENILs prepared with increasing load of EtOHmimBF₄ ($R_{0.5}$–$R_4$).

![Fig. 3](image3.png)  (A) Dynamic thermogravimetric curve (TGA) of neat EtOHmimBF₄ and $C_{cap}$, (B) normalized derivative thermogravimetric curve (DTG) of ENILs prepared with EtOHmimBF₄ and neat EtOHmimBF₄ (nitrogen atmosphere and a heating rate of 10 °C min⁻¹).
collects the operating conditions and the main results extracted from the NH₃ capture experiments conducted, including the breakthrough time (tᵃ), the saturation capacity (qₛ) calculated on different basis, and the length of mass transfer zone (h_MSB). Ccap support presents a high NH₃ uptake per mass of sorbent (qₛ, sorb = 6.0 mg g⁻¹), equivalent and even higher than those reported for physical adsorption with ACs. The operating temperature has a remarkable effect on NH₃ adsorption by Ccap, with bed capacity decreasing by ~40% when temperature increased from 30 to 60 °C. This change is in agreement with the results obtained for NH₃ adsorption with other ACs in bibliography. The length of mass transfer zone values (e.g. h_MSB = 1.5 cm at 30 °C) are close to the values reported for the adsorption of other solutes (chloromethanes, ethanol) on ACs. This reveals fast and favorable NH₃ adsorption onto Ccap, ascribable to the large contact surface area and low size of the submicrocapsules.

Fig. 5 presents the NH₃ breakthrough curves obtained in fixed bed experiments using ENIL–Rₙ prepared with different loads of EtOHmimBF₄, being the main results extracted from them and collected in Table 4. As can be seen, the incorporation of the IL into the Ccap support does not improve the sorption capacity per unit mass of sorbent (qₛ,ENIL). However, due to filling of the pores of Ccap with IL, the NH₃ sorption capacity per bed volume unit (qₛ,VI cm⁻³) evidences the advantages of ENILs in terms of bed efficiency when compared to Ccap. Thus, when the load of EtOHmimBF₄ in the ENILs is increased, the total amount of NH₃ captured by the bed was higher, with the breakthrough times increasing from 8.6 to 22.7 minutes for R₉,₅ and R₉, respectively. These tests were carried out using approximately the same length of bed (4.8–5.1 cm), which

![Graph](image-url)

**Fig. 4** Breakthrough curves of NH₃ sorption by fixed bed of Ccap (2000 ppmv inlet NH₃ concentration, 20 mL min⁻¹ and a bed length of 5 cm).

| T, °C | [NH₃]₀ (ppmv) | h, cm | m, ENIL (mg) | tᵃ (min) | qₛ,VI (mg cm⁻³) | qₛ,ENIL (mg g⁻¹) | h_MSB (cm) |
|------|---------------|------|-------------|----------|----------------|-----------------|-----------|
| Ccap | 30 | 2000 | 4.8 | 52.2 | 9.9 | 0.52 | — | 6.0⁶ |
| ENIL–R₉,₅ | EtOHmimBF₄ | 30 | 2000 | 4.9 | 77.0 | 8.6 | 0.48 | — | 3.8 |
| ENIL–R₉ | EtOHmimBF₄ | 30 | 2000 | 5.0 | 119.6 | 11.6 | 0.61 | — | 3.2 |
| ENIL–R₉ | EtOHmimBF₄ | 30 | 2000 | 5.1 | 164.7 | 12.8 | 0.77 | — | 3.0 |
| ENIL–R₉ | EtOHmimBF₄ | 30 | 2000 | 5.8 | 216.4 | 22.7 | 1.18 | 4.1 | 3.3 |
| ENIL–R₉ | CholineNTf₂ | 30 | 2000 | 4.7 | 236.0 | 8.9 | 0.48 | 1.5 | 1.2 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 30 | 2000 | 4.3 | 209.0 | 9.9 | 0.62 | 2.0 | 1.6 |
| Ccap | 45 | 2000 | 5.0 | 49.2 | 7.0 | 0.42 | — | 5.4 |
| ENIL–R₉ | EtOHmimBF₄ | 45 | 2000 | 4.8 | 214.0 | 21.9 | 1.10 | 3.9 | 3.1 |
| ENIL–R₉ | CholineNTf₂ | 45 | 2000 | 4.5 | 231.5 | 8.9 | 0.49 | 1.4 | 1.2 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 45 | 2000 | 4.0 | 207.7 | 7.1 | 0.50 | 1.5 | 1.2 |
| Ccap | 60 | 2000 | 5.0 | 50.0 | 4.9 | 0.30 | — | 3.8 |
| ENIL–R₉ | EtOHmimBF₄ | 60 | 2000 | 4.7 | 214.0 | 19.3 | 1.01 | 3.5 | 2.8 |
| ENIL–R₉ | CholineNTf₂ | 60 | 2000 | 4.5 | 231.2 | 8.1 | 0.45 | 1.3 | 1.1 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 60 | 2000 | 4.0 | 205.0 | 4.1 | 0.33 | 1.0 | 0.8 |
| ENIL–R₉ | EtOHmimBF₄ | 30 | 500 | 4.4 | 192.0 | 74.9 | 0.76 | 2.8 | 2.2 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 30 | 800 | 4.3 | 195.4 | 44.9 | 1.08 | 3.7 | 3.0 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 30 | 1200 | 4.5 | 198.0 | 35.7 | 1.12 | 3.9 | 3.2 |
| ENIL–R₉ | CholineNTf₂ | 30 | 1500 | 4.4 | 194.0 | 33.0 | 1.12 | 3.9 | 3.2 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 30 | 500 | 4.3 | 224.5 | 28.8 | 0.29 | 1.1 | 0.7 |
| ENIL–R₉ | CholineNTf₂ | 30 | 800 | 4.3 | 225.0 | 19.6 | 0.42 | 1.3 | 1.0 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 30 | 1200 | 4.4 | 222.5 | 9.9 | 0.44 | 1.3 | 1.1 |
| ENIL–R₉ | [EtOH]₃MeNMeSO₄ | 30 | 1500 | 4.4 | 225.8 | 9.6 | 0.45 | 1.4 | 1.1 |

* Mixture of adsorption and absorption phenomena. The notation qₛ, sorb (mg g⁻¹ Ccap adsorbent⁻¹).
It is noticeable that the NH₃ sorption capacity per unit mass of IL of the ENIL–R₄ prepared with EtOHmimBF₄ (qₐ₄₃ = 4.1 mg g⁻¹) is close to the absorption capacity of neat EtOHmimBF₄ (qₐ₄₃ = 4.40 mg g⁻¹; see Fig. S4 in ESI†) obtained by gravimetric measurements at identical temperature and NH₃ concentration. It indicates that the task-specific IL maintains its high NH₃ absorption capacity after encapsulation.

Fig. 6 compares the breakthrough curves obtained for ENIL–R₄ prepared with the different ILs (EtOHmimBF₄, CholineNTf₂ and (EtOH)₃MeNMeSO₄) at temperatures of 30, 45 and 60 °C. The NH₃ capacity per bed volume unit (qₐₘ₃ mg cm⁻³, Table 4) at 30 °C increases in the order EtOHmimBF₄ > (EtOH)₃MeNMeSO₄ > CholineNTf₂, in good agreement with the absorption capacities of the corresponding neat ILs (see Fig. S4 in ESI†). This confirms that the selection of the task-specific IL also plays a crucial role in the NH₃ capture by ENIL in fixed-bed operation.

Increasing the temperature from 30 to 60 °C resulted in lower bed capacities, as can be seen from the shift of the breakthrough curves to shorter times and the parameters summarized in Table 4. It should be remarked that the NH₃ uptakes achieved with ENILs prepared with EtOHmimBF₄ and (EtOH)₃MeNMeSO₄ were less affected by temperature than in the case of Ccap (Fig. 4). The low influence of temperature may be ascribed to the low enthalpy associated to the physical absorption of NH₃ (ca. 5 kJ mol⁻¹ for IL EtOHmimBF₄) in comparison with the physical adsorption of NH₃ on AC (ca. 25 kJ mol⁻¹). Therefore, the bed efficiency (qₐₘ₃ in mg cm⁻³) is less affected by temperature in the case of these ENILs (~15% variation in 30–60 °C temperature range) than for Ccap (~40% variation in 30–60 °C temperature range) and more flexibility can be achieved for operation at different temperatures. This adverse temperature effect on NH₃ adsorption has been previously observed in commercial carbonaceous adsorbents: BAHICARBON AC (~50% variation in 40–80 °C temperature range) and MERCK AC (~50% variation in 25–55 °C temperature range). The ENIL prepared with CholineNTf₂ is barely affected by the temperature in the range considered. This behavior is related to the fact that CholineNTf₂ melts at 30 °C and the solid state polymorphism can affect the capture experiments at surrounding temperatures.
Fig. 7 compares the NH₃ sorption capacity of ENILs in terms of the amount retained per g of IL (\(q_{s,IL; m g g^{-1} IL/C_0}\)) and the amount retained per bed volume unit (\(q_{s,V; m g cm^{-3}/C_0}\)). As can be seen, the relationship between these two parameters is almost linear, indicating that the absorption capacity of neat ILs can be considered as the main reference parameter for selecting ILs to prepare effective ENIL sorbents for a specific gas treatment. This linear relationship is also nearly independent of the IL used, since the three ones here considered have similar density (Table 2).

Fig. 8 depicts the NH₃ sorption isotherms (\(q_{s, ENIL; m g g_{ENIL}^{-1}}\)) at 30 °C for ENILs–R₄ prepared with EtOHmimBF₄, (EtOH)₃MeNMeSO₄ and CholineNTf₂, as calculated from the breakthrough curves obtained at different NH₃ inlet concentration (Fig. 5S of ESI†). The amount of ammonia retained generally increases with increasing inlet NH₃ partial pressures, in concordance with the absorption isotherms obtained for neat ILs. The results show again the significantly higher NH₃ sorption capacity of the ENIL–R₄ prepared with EtOHmimBF₄.

The length of mass transfer zone (\(h_{MTZ}\)) is an additional parameter of interest to evaluate the performance of NH₃ capture by ENILs. The values obtained ENIL (see Table 4) indicate that, interestingly, the incorporation of IL into the Ccap has only minor effect on the slope of breakthrough curves and \(h_{MTZ}\) values at 30 °C, showing that the good mass transfer conditions are maintained. Increasing the sorption temperature evidences additional advantages of ENILs, since \(h_{MTZ}\) decreased for all ENIL sorbents prepared. This effect is assignable to the higher NH₃ diffusivity in ILs at higher temperatures. On the contrary, \(h_{MTZ}\) increases with temperature for Ccap (see Table 4), which is the commonly reported effect of temperature on the adsorption of gases by porous carbons. In fact, comparison to available data of NH₃ fixed bed adsorption using commercial AC (BAHIACARBON, \([NH_3]_0 = 1200 \text{ ppmv, 1 atm}\)) leads to similar conclusions, with estimated \(h_{MTZ}\) values of 1.8 and 2.8 cm at 40 and 80 °C, respectively.

### 3.3. Process reversibility

The last step in this study was the evaluation of the regeneration of the exhausted ENILs, since it is an important issue regarding the potential application to NH₃ capture. Fig. 9 shows the NH₃ capture capacities (\(q_{s, ENIL; m g g_{ENIL}^{-1}}\)) of the ENILs prepared with the three ILs (EtOHmimBF₄, CholineNTf₂ and (EtOH)₃MeNMeSO₄), calculated from breakthrough curves obtained in 3 successive capture-regeneration cycles. As can be seen, the sorption capacity of the ENILs remains nearly unaltered after the regeneration, thus showing the reusability of the bed. The
effective regeneration is another main advantage of ENILs to conventional adsorbents, since the desorption of NH\textsubscript{3} from porous solid is a main concern.\textsuperscript{63}

4. Conclusions

Encapsulated ionic liquids (ENILs) were specifically designed for NH\textsubscript{3} capture from gas effluent, with further recovery of this compound, and their performance was evaluated by means of fixed bed experiments. The confinement of task-specific ILS into the carbon submicrocapsules resulted in ENILs with high IL content (up to 85\% w/w), high NH\textsubscript{3} uptake capacity and high thermal stability (this last very close to that of neat IL). The incorporation of the ILS into the carbon submicrocapsules hollow space increased the efficiency of the bed (capacity per bed volume unit), respect to the benchmark carbonaceous adsorbent (C\textsubscript{cap} or commercial activated carbons). The large surface contact area of submicrocapsule particles promotes high mass transfer rates for NH\textsubscript{3} sorption in ENILs. As a result, the lengths of the mass transfer zone obtained in fixed bed experiments with ENILs are similar or even shorter than those obtained with common adsorbents, indicating an efficient use of ENILs in the fixed bed. The application of ENILs in fixed bed operations may be particularly advantageous at higher temperatures, from both thermodynamic and kinetic points of view, respect to carbonaceous adsorbents. In addition, ENILs were successfully regenerated under mild conditions and used in successive NH\textsubscript{3} capture-desorption cycles, without loss of operation efficiency. This a clear advantage respect to common gas adsorbents, which in general have problems of regeneration at mild conditions. The current results present ENILs as new separating agents with promising characteristics for future practical applications.

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