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Efficient and Reversible Absorption of Ammonia by Cobalt Ionic Liquids through Lewis Acid-Base and Cooperative Hydrogen Bond Interactions

Shaojuan Zeng^a, Lei Liu^b, Dawei Shang^{a, c}, Jiangpeng Feng^{a, c}, Haifeng Dong^a, Qiuxia Xu^a,

Xiangping Zhang^{a,c,*}, Suojiang Zhang^a

^a Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex System, Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China

^b Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn Beringstr. 4, 53115 Bonn, Germany

^c College of Chemical and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

^{*}Corresponding author. Tel./fax: +86-010-82544875

E-mail address: xpzhang@ipe.ac.cn

ABSTRACT

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Ammonia (NH₃) emissions have caused a wide range of environmental problems and serious harm to human health. However, efficiently separating NH₃ and simultaneously recovering high purity of NH₃ easily remains a great challenge. A new strategy to design transition metal ionic liquids (MILs) by combing specific metal centers and ligands with ILs was proposed for efficient and reversible absorption of NH₃. Not only exceptional NH₃ absorption capacity and high NH₃/CO₂ selectivity, but also excellent recyclability were achieved by the cobalt ILs [C_nmim]₂[Co(NCS)₄]. The maximal capacity of NH₃ is up to 6.09 molNH₃·molIL⁻¹ at 30°C and 0.10 MPa, which is much higher than all reported ILs to date, and is over 30 times higher than the conventional ILs [C_nmim][SCN]. The superior NH₃ capacity and desorption performance is originated from the moderate Lewis acid-base and cooperative hydrogen bond interactions between the metal centers-ligands and NH₃.

Keywords: Cobalt ionic liquids, Ammonia absorption, Lewis acid-base interaction, Hydrogen bond

1. Introduction

Emission of toxic gases and greenhouse gases is a serious problem in the establishment of a sustainable society and is driving the implementation of green chemistry concepts. Therefore, gas separation and purification as an everlasting research topic has already attracted extensive attentions worldwide^{1, 2}. As one of the typical alkaline and poisonous pollutants, ammonia (NH₃) is widely considered to be a primary factor for the formation of fog and haze, which has been seriously hazarding environment and human health for a long time³. On the other hand, NH₃ is also an important raw material and applied in various fields, such as fertilizer, freezing medium⁴. Therefore, a few technologies for NH₃ separation, like water scrubbing and acid scrubbing, have been applied in industries. However, some inherent drawbacks come with yet. For example, water scrubbing consumes a large amount of water to reach ultra-low NH₃ emission requirements (lower than 10 mg·m⁻³), and finally obtains low concentration of aqueous ammonia (less than 3 wt%), which incurs great difficulties for NH3 desorption and recycle. Acid scrubbing produces huge amounts of irreversible ammonium salts as low value-added products and wastewater that doesn't follow the principles of green chemistry. Hence, the development of green techniques for efficiently separating and recovering NH₃ is of critical significance.

Ionic liquids (ILs) have caught considerable attentions as competitive alternatives in SO₂, CO₂ and NH₃ separation owing to their peculiar properties, like extremely low vapour pressure, high thermal stability and tuneable properties⁵⁻¹². It is reported that

NH₃ has optimistic solubility in most conventional ILs, and the cation plays a greater role in NH₃ absorption than the anion¹³⁻¹⁸, which differs from the case for acid gases such as $SO_2^{19, 20}$ and CO_2^{21-25} . Comparing with other cations such as pyrrolodinium, quinolinium, and phosphonium, imidazolium-based ILs show higher NH₃ capacity²⁶. Furthermore, the introduction of hydroxyl groups into cations can substantially improve NH₃ capacity due to hydrogen bonding between the hydroxyl group and NH₃^{8, 27}. For example, NH₃ solubilities in 1-2(-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([EtOHmim][BF₄]) and choline bis(trifluoromethylsulfonyl)imide ([Choline][Tf₂N]) were 1.70 and 1.86 molNH₃·molIL⁻¹ at 20 °C and 0.10 MPa, respectively, whereas that in [Emim][BF₄] was only 0.28 molNH₃·molIL⁻¹. Recently, al.¹⁸ reported that a novel protic IL 1-butylimidazolium Shang et bis(trifluoromethylsulfonyl)imide ([Bim][Tf₂N]) absorbs 2.69 molNH₃·molIL⁻¹ at 40°C and 0.10 MPa through the strong hydrogen bonding between NH₃ and cations. Xing et al.²⁸ also designed the hybrid deep eutectic solvents with high NH₃ capacity of 0.13 gNH_3 gabsorbent⁻¹ at 40°C and 0.10 MPa through a flexible hydrogen-bonded supramolecular network. However, these physisorption ILs are still unable to compete with the traditional absorbents. For this reason, an alternative approach has been proposed, that is chemisorption, which is normally accomplished by the incorporation of metal centers. Metal chlorides as chemical adsorbents show higher capacity of NH₃ adsorption than that in water, but metal chloride-NH₃ systems have poor heat transfer performance and attenuation of adsorptive capacity due to their irreversibility²⁹. Kohler et al.³⁰ prepared novel spherical activated carbon support materials containing

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copper(II) salts, and found that the copper(II)-based materials show better NH_3 adsorption performance by combining chemical and physical interaction than that of the metal-free materials. However, the common drawback for these materials is the formation of strong chemical interactions between metal centers and gas molecules, which makes it impossible to regenerate NH_3 and reuse the adsorption materials. Therefore, an appropriate balance and tradeoff between the absorption capacity and desorption ability must be considered to design novel absorbents for highly efficient and reversible absorption of NH_3 .

In this work, we proposed a new strategy to achieve high performance on both NH₃ absorption and desorption using transition metal ILs (MILs) through the Lewis acid-base and hydrogen bonding interaction between metal centers-ligands and NH₃. The key of desiging MILs is to screen the suitable metal centers and ligands, which can react with NH₃ forming high coordination structures (e.g. octahedron) with moderate stability constants (Table S1). Besides, the MILs should keep in a liquid state before and after NH₃ absorption under the temperature (\leq 50°C), and have good flowability, which is favorable for the transport and kinetic aspects of NH₃ absorption. Thus, the cobalt ILs [C_nmim]₂[Co(NCS)₄] (n=2, 4, 6) were designed and synthesized for efficient and reversible absorption of NH₃. The physicochemical properties of ILs (density, viscosity, thermal decomposition temperatures and glass transition temperatures), the effect of temperature, pressure and water contents on NH₃ absorption performance as well as NH₃ selectivity and the regeneration and recyclability of ILs were systematically investigated. Moreover, the mechanism of

 NH_3 absorption in $[C_nmim]_2[Co(NCS)_4]$ was well explained through both experimental characterizations and Quantum Chemical calculations.

2. Experiment

2.1. Materials

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NH₃ (99.999%), CO₂ (99.999%) and N₂ (99.99%) were supplied by Beijing Beiwen Gas Factory. [Emim]Cl, [Bmim]Cl and [Hmim]Cl (> 99.0%) were supplied by Linzhou Keneng Material Technology Co. Ltd. Cobalt (II) chloride, anhydrous (CoCl₂, 97.0%) was obtained from Sinopharm Chemical Reagent Co., Ltd. Other chemical reagents of analytical grade, including acetone, dichloromethane, kalium thiocyanate (KSCN) were purchased from Beijing Chemical Company.

2.2. Synthesis and characterizations of ILs

Two kinds of ILs including three conventional ILs $[C_n mim][SCN]$ and three MILs $[C_n \text{mim}]_2[Co(\text{NCS})_4]$ (n=2, [Emim], 1-ethyl-3-methylimidazolium; n=4, [Bmim], 1-butyl-3-methylimidazolium; n=6, [Hmim], 1-hexyl-3-methylimidazolium. [SCN], thiocyanate, and $[Co(NCS)_4]^{2-}$, tetraisothiocyanatocobaltate(II)) were synthesized by a one-step method. The conventional ILs $[C_nmim][SCN]$ including 1-ethyl-3-methylimidazolium thiocyanate ([Emim][SCN]), 1-butyl-3-methylimidazolium thiocyanate ([Bmim][SCN]), 1-hexyl-3-methylimidazolium thiocyanate ([Hmim][SCN]), were synthesized following the reported methods^{5, 6}. Taking [Bmim][SCN] as an example, the anion exchange reaction was performed by mixing [Bmim]Cl and equimolar KSCN in

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acetone. After stirring for 48 h at room temperature, the mixture was filtered and washed with acetone. The organic layer was collected and concentrated by rotary evaporation to remove the solvent. Then the raw product with dichloromethane was frozen for 3~5 h under -5°C. After filtration and removal of solvents, the final product [Bmim][SCN] was obtained as the dark orange liquid under vacuum at 50°C for 48 h. [Emim][SCN] and [Hmim][SCN] were synthesized in the same method expect the [Bmim]Cl was substituted by [Emim]Cl and [Bmim]Cl, respectively.

The cobalt ILs $[C_n mim]_2[Co(NCS)_4]$ were synthesized by mixing CoCl₂ and KSCN in an acetone solution of [Bmim]Cl through the anion-exchange method. In the typical experiment, 8.000 g CoCl₂ (0.062 mol), 23.951 g KSCN (0.246 mol) and 21.526 g [Bmim]Cl (0.123 mol) were added into 100 ml acetone and stirred 48 h at room temperature. After filtration and removal of the solvents by rotary evaporation, the resulting product was washed with dichloromethane, and dried under vacuum at 50°C for 48 h to afford [Bmim]_2[Co(NCS)_4] as the blue liquid. [Emim]_2[Co(NCS)_4] and [Hmim]_2[Co(NCS)_4] were synthesized in an analogous manner, using [Emim]Cl and [Bmim]Cl instead of [Bmim]Cl, respectively. Elemental analysis (%) calculated for [Emim]_2[Co(NCS)_4]: C 37.42, H 4.32, N 21.82; Found: C 37.69, H 4.29, N 21.74; For [Bmim]_2[Co(NCS)_4]: C 42.17, H 5.31, N 19.56; Found: C 42.05, H 5.40, N 19.67; For [Hmim]_2[Co(NCS)_4]: C 46.09, H 6.09, N 17.92; Found: C 46.26, H 6.27, N 17.46.

All the ILs were dried under vacuum at 50°C for 48 h before use. The FT-IR spectra were recorded by a Thermo Nicolet 380 Spectrometer to confirm the structures of the studied ILs. The structures of three conventional ILs ([Emim][SCN],

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[Bmim][SCN] and [Hmim][SCN]) were confirmed by ¹H NMR and ¹³C NMR spectroscopy (see the supporting information) with Bruker 600 spectrometer. UV/vis spectra in the range of 200-900 nm were recorded using UV-Vis spectrophotometer (UV-2550). Measurements were done on the solutions of $[C_n mim]_2[Co(NCS)_4]$ in acetone, and the absorption maximum of $[C_n \text{mim}]_2[Co(\text{NCS})_4]$ in acetone were 623 and 587 nm. The water contents in the ILs after drying were determined with volumetric Karl Fischer Titration (Metrohm, 787 KF Titrino) and found to be less than 0.01 wt%. The residual halide contents in the ILs were measured using PXSJ-226 Series Ion meter (INESA Scientific Instrument Co. Ltd), and found to be less than 0.02 wt%. The density and viscosity of ILs were measured from 20 to 70°C with a density meter (Anton Paar DMA 5000) and an automated microviscometer (Anton Paar AMVn), respectively. Decomposition temperatures were determined by thermogravimetric analysis (TGA Q5000) by heating from room temperature to 600°C under nitrogen atmosphere with heating rate of 10 °C·min⁻¹. The glass transition temperature of ILs was measured by differential scanning calorimeter (Mettler Toledo DSC1) from -150 to 50 °C under nitrogen atmosphere with heating rate of 10 °C \cdot min⁻¹.

2.3. NH₃ absorption and desorption

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NH₃ absorption and desorption experiments followed the same procedures of our previous work^{5, 6, 31}. In a typical absorption, NH₃ gas of atmosphere pressure is bubbled through about 5 g ILs in the glass container with an inner diameter of 3.0 cm at a flow rate of 140 ml·min⁻¹. The glass container was partly immersed in a circulated water bath at the desired temperature within \pm 0.10°C. The amount of NH₃ absorbed

in the IL was measured at different times by an electronic balance with an accuracy of ± 0.10 mg, and was finally determined according to the increase of the weight. For NH₃ absorption under reduced pressure, the NH₃ partial pressure was adjusted by changing the flow of NH₃ and N₂. For NH₃ desorption, NH₃ was desorbed by heating and bubbling N₂ through IL solutions with saturated NH₃. In this study, pure N₂ gas with the same flow rate was bubbled through the IL with absorbed NH₃ in the glass container at 80°C, and the amount of NH₃ desorption was also determined at regular intervals by an electronic balance until the weight kept constant. The reproducibility of the absorption and desorption experiments was less than $\pm 3\%$, and it was estimated that the experimental error involved in the method was at the level of $\pm 5\%$.

2.4. Computational methods

All density functional theory (DFT) calculations were performed by employing Turbomole 7.0 software³². The structures were optimized at the TPSS level of theory³³, with the BJ-damped variant of the DFT-D3 dispersion correction³⁴ in conjunction with the def2-TZVP basis set^{35, 36}. Harmonic vibrational frequency calculations were conducted at the same level to characterize the nature of the stationary points along the reaction coordinates: no imaginary frequencies were found for the local minima, and one and only one imaginary frequency was found for the transition state. The thermostatistical contributions to the Gibbs energy in the gas phase were obtained from a modified rigid-rotor-harmonic oscillator approximation³⁷ at temperatures of 25°C and 1 atm pressure. The density-fitting RI-J³⁸ approach for the Coulomb integrals was used to accelerate the geometry optimization and

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frequencies calculations. Accurate electronic energies were obtained from single point calculations upon the optimized structures at both the hybrid metal PBE0-D3 functional³⁹ with the basis set of def2-TZVPP. The COSMO-RS (Conductor-like Screening Model for Real Solvents) solvation model^{40, 41} was used to compute the solvation Gibbs energies by employing the gas–phase optimized structures, and with ILs as the solvent. These calculations were done with the COSMOtherm program⁴².

3. Results and discussion

3.1. Physicochemical properties of ILs

Density and viscosity of ILs are two fundamental parameters for screening and evaluation of ILs for gas separation. Therefore, Densities and viscosities of the conventional ILs [C_nmim][SCN] and the cobalt ILs [C_nmim]₂[Co(NCS)₄] in the temperature range from 20 to 70°C were studied as shown in Figure 1. Comparing with [C_nmim][SCN], [C_nmim]₂[Co(NCS)₄] with doubly charged anions have much higher densities and viscosities. For instance, the density and viscosity of [Bmim][SCN] were 1.08 g·cm⁻³ and 83.71 mPa·s at 20°C, whereas those of [Bmim]₂[Co(NCS)₄] increased to 1.22 g·cm⁻³ and 480.41 mPa·s, respectively. However, the viscosities of [C_nmim]₂[Co(NCS)₄] are much lower than those of other reported MILs. Most MILs with transition metal halide anions are solid at room temperature due to the extensive hydrogen-bonding network⁴³. Only a few of MILs, like [FeCl₄]⁻-based ILs, and phosphonium-based ILs containing different metal halide

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anions at room temperature are liquid, and their viscosities are extremely high, with the maximum of 123500 mPa·s at $20^{\circ}C^{44}$. The lower viscosities of $[C_n \text{mim}]_2[Co(NCS)_4]$ in this work may be due to the weaker interactions between soft pseudo-halide anions and the hard hydrogen atoms of the imidazolium cations than the halogen groups⁴⁵.



Figure 1. Variation in the densities (a) and viscosities (b) of ILs with temperature:

[Emim]₂[Co(NCS)₄]; ●, [Bmim]₂[Co(NCS)₄]; ▲, [Hmim]₂[Co(NCS)₄]; □, [Emim][SCN]; ○,

[Bmim][SCN]; Δ, [Hmim][SCN].

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In addition, the thermal properties including thermal decomposition temperatures (T_d) and glass transition temperatures (T_g) of $[C_nmim][SCN]$ and $[C_nmim]_2[Co(NCS)_4]$ were also studied. As shown in Table 1, the presence of anionic transition-metal thiocynate complexes plays an important role in thermal properties of ILs. The thermal decomposition temperatures of the cobalt ILs are all above 280°C, and much higher than those of $[C_nmim][SCN]$, indicating that $[C_nmim]_2[Co(NCS)_4]$ exhibit more excellent thermal stability. Moreover, no melting points were detected for $[C_nmim]_2[Co(NCS)_4]$, but glass transition temperatures was around -63°C.

ILs	${}^{a}T_{d}/{}^{\circ}C$	T _g /℃
[Emim] ₂ [Co(NCS) ₄]	302.8	-63.22
[Bmim] ₂ [Co(NCS) ₄]	300.0	-62.91
[Hmim] ₂ [Co(NCS) ₄]	288.4	-62.57
[Emim][SCN]	230.4	-101.13
[Bmim][SCN]	229.3	-92.70
[Hmim][SCN]	228.9	-91.28

Table 1. Thermal decomposition temperatures and glass transition temperatures of ILs

 ${}^{a}T_{d}$ is defined as the temperature at which the IL loses 5% of its initial mass while heating from room temperature to 600°C with a heating rate of 10°C ·min⁻¹ under N₂ atmosphere.

3.2. NH₃ absorption by cobalt ILs

In order to study the effect of the anionic transition-metal complex $[Co(NCS)_4]^2$ with thiocynate ligands on NH₃ absorption, NH₃ capacity by the cobalt ILs $[C_nmim]_2[Co(NCS)_4]$ and the conventional ILs $[C_nmim][SCN]$ as a function of time

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was studied and shown in Figure 2. It was found that all the cobalt ILs $[C_n \min]_2[C_0(NCS)_4]$ exhibited very high NH₃ capacity, which can absorb 5.99~6.09 molNH₃·molIL⁻¹ at 30°C and 0.10 MPa. However, the maximal NH₃ capacity by the conventional ILs [C_nmim][SCN] is only 0.20 molNH₃·molIL⁻¹ under the same conditions. This means that NH₃ capacity by $[C_n mim]_2[Co(NCS)_4]$ is over 30 times than that of in the corresponding metal-free ILs $[C_n mim][SCN]$. When the cation varied from [Emim]₂ to [Bmim]₂ and [Hmim]₂, NH₃ capacity of the cobalt ILs increased slightly from 5.99 to 6.03 and 6.09 molNH₃ molIL⁻¹, respectively. The similar results are obtained using $[C_n mim][SCN]$, implying the minor influence of the alkyl chain length of the cation on NH₃ capacity. Therefore, significant improvement in NH₃ absorption by $[C_n \text{mim}]_2[C_0(\text{NCS})_4]$ is mostly attributed to the strong interaction between the anion and NH₃, which is different from the mechanism of NH₃ physisorption in ILs^{8, 16, 18}. Meanwhile, the molar ratio between NH₃ and the amount of cobalt(II) ion also indicates the formation of $[Co(NH_3)_6]^{2+}$ complexes through chemical complexation.



Figure 2. NH₃ and CO₂ absorption behaviors of [C_nmim]₂[Co(NCS)₄] and [C_nmim][SCN] at 30 °C

and 0.10 MPa

3.3. NH₃ selectivity in cobalt ILs

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There are always other gases accompanied with NH₃ in real industries, such as low concentration of CO₂ in the tail gases of urea or ammonium bicarbonate plants. Therefore, selectively separating NH₃ from gas mixtures becomes particularly important. Table 2 listed the NH₃ and CO₂ capacity and NH₃/CO₂ selectivity in $[C_nmim]_2[Co(NCS)_4]$ and $[C_nmim][SCN]$, respectively. The results showed that $[C_nmim]_2[Co(NCS)_4]$ exhibit much higher NH₃/CO₂ selectivity in the range from 39.0 to 52.5, whereas the NH₃/CO₂ selectivity are lower than 7 for the corresponding $[C_nmim][SCN]$, indicating that $[C_nmim]_2[Co(NCS)_4]$ can effectively and selectively separate NH₃ from mixture gas containing CO₂.

	Molgas·mo	NH ₃ /CO ₂		
ILs	NH ₃	CO ₂	selectivity	
[Emim] ₂ [Co(NCS) ₄]	5.99	0.114	52.5	
[Bmim] ₂ [Co(NCS) ₄]	6.03	0.129	46.7	
[Hmim] ₂ [Co(NCS) ₄]	6.09	0.156	39.0	
[Emim][SCN]	0.18	0.028	6.4	
[Bmim][SCN]	0.19	0.042	4.5	
[Hmim][SCN]	0.20	0.058	3.4	

Table 2. NH₃/CO₂ selectivity in [C_nmim]₂[Co(NCS)₄] and [C_nmim][SCN]

^aThe absorption experiment was carried out at 30°C and 0.10 MPa.

3.4. Effect of water on NH₃ absorption

Besides, water is also inevitably present in industrial gases. Hence, saturated water contents of ILs by mass fraction at 30 °C were measured, and the effect of water in ILs on NH₃ absorption at 30 °C and 0.10 MPa was also investigated. It was found that $[C_nmim]_2[Co(NCS)_4]$ has low saturated water contents in the range of 0.97 to 1.77 wt%, and become gradually hydrophobic with the increasing alkyl chain length of the imidazodium cation. The addition of the small amounts of water (less than 2.0 wt%) into $[C_nmim]_2[Co(NCS)_4]$ has the slight negative impact in NH₃ capacity. For example, when the water content in $[Bmim]_2[Co(NCS)_4]$ increases to 1.22 wt%, the NH₃ capacity decreases to 0.172 gNH₃·gIL⁻¹, which corresponds to 4.44% reduction in NH₃ capacity. As the water content in $[Bmim]_2[Co(NCS)_4]$ is about 0.66 wt%, the

 NH_3 capacity is nearly close to that of the pure IL. However, the presence of water could reduce the viscosity of the cobalt ILs obviously, which is helpful for improving the gas-absorption kinetics in these ILs^{46} .

ILs	Water contents	^a g NH ₃ ·g IL ⁻¹	^b g NH ₃ ·g IL ⁻¹
[Emim] ₂ [Co(NCS) ₄]	1.77% ^c	0.192	0.198
[Bmim] ₂ [Co(NCS) ₄]	1.22% ^c	0.172	
[Bmim] ₂ [Co(NCS) ₄]	1.06%	0.175	0.180
[Bmim] ₂ [Co(NCS) ₄]	0.66%	0.179	
[Hmim] ₂ [Co(NCS) ₄]	0.97% ^c	0.155	0.166

Table 3. Saturated water contents and NH₃ capacity in [C_nmim]₂[Co(NCS)₄] with water

^aCobalt ILs with water. ^bPure cobalt ILs. ^cSaturated water contents of cobalt ILs.

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3.5. Effect of temperature and pressure on NH₃ absorption

Moreover, $[Bmim]_2[Co(NCS)_4]$ was selected as an example to further investigate the effect of temperature and pressure on NH₃ absorption. As shown in Figure 3, both the temperature and the pressure play a significant role in NH₃ absorption. The mass ratio of NH₃ to IL for $[Bmim]_2[Co(NCS)_4]$ decreased continuously from 0.18 to 0.063 with an increase of temperature from 30 to 80°C, and increased from 0.052 to 0.18 with the increasing partial pressure of NH₃ from 0.01 to 0.10 MPa. When the partial pressure was 0.005 MPa, the mass ratio of NH₃ to $[Bmim]_2[Co(NCS)_4]$ was 0.018, which is even higher than that in several conventional ILs at 0.10 MPa^{14, 16}, indicating that the cobalt ILs is suitable for low concentration of NH₃ absorption. The NH₃

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capacity in $[Bmim]_2[Co(NCS)_4]$ increases with the increasing pressure and the decreasing temperature. Thus, the absorbed NH₃ in the cobalt ILs can be easily released by heating or/and reducing the partial pressure of NH₃.



Figure 3. Effect of temperature (a) and pressure (b) on NH₃ absorption by [Bmim]₂[Co(NCS)₄]

3.6. Regeneration and recycle of cobalt ILs

In order to examine the regeneration and recyclability of the cobalt ILs $[C_n mim]_2[Co(NCS)_4]$, five consecutive absorption-desorption experiments by

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 $[Bmim]_2[Co(NCS)_4]$ were further investigated. As seen in Figure 4, all the NH₃ absorbed can be easily released as the IL-NH₃ complexes are exposed to reduced pressure and relatively high temperature. Importantly, no changes have been observed on the structures of the cobalt ILs after NH₃ desorption, and the IR spectra are almost identical to that of the fresh cobalt ILs (Figure S10). Furthermore, $[Bmim]_2[Co(NCS)_4]$ can be recycled and exhibit no significant loss in NH₃ capacity after five complexation-evolution cycles, implying that the process is completely reversible. Meanwhile, the multiple absorption and desorption of NH₃ by $[Bmim]_2[Co(NCS)_4]$ with saturated water (1.22 wt%) was also investigated (Figure S9). Similarly, the absorption performance of NH₃ by $[Bmim]_2[Co(NCS)_4]$ with water after five cycles also remains stable. However, the absorbed NH₃ is more easily and faster desorbed from $[Bmim]_2[Co(NCS)_4]$ with water than the pure IL under the same conditions.

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Figure 4. Five consecutive cycles of NH_3 absorption and desorption by $[Bmim]_2[Co(NCS)_4]$. NH_3 absorption was carried out at 30 °C and 0.10 MPa, and NH_3 desorption at 80 °C under N_2 .

Absorption \blacksquare , desorption \square

3.7. The mechanism for NH₃ absorption

All the results discussed above demonstrated that the $[C_n mim]_2[Co(NCS)_4]$ not only have higher capacity of NH₃ absorption, but also exhibit excellent recyclability. Why do the cobalt ILs $[C_n mim]_2[Co(NCS)_4]$ exhibit such high capacity and excellent regeneration performance? In order to explain the NH₃ absorption and desorption mechanism with $[C_n mim]_2[Co(NCS)_4]$, the optimized structures of NH₃ and CO₂ with the SCN⁻ and Co(NCS)₄²⁻ anions by DFT calculations were depicted in Figure 5. The shortest distance between the gases (CO₂ and NH₃) and SCN⁻ are 2.6 Å and 2.7 Å, respectively (Figure 5(a) and 5(b)). The computed reaction Gibbs free energies ΔG are -0.1 kcal·mol⁻¹ and 0.8 kcal·mol⁻¹ for NH₃ and CO₂ absorption, respectively, which are in the range of typical binding affinity of physisorption. The calculated NH₃/CO₂ selectivity is 4.6, which is in good agreement with the experimental values (Table 2).

For the Co(NCS)₄²⁻ anion, six NH₃ molecules replace four SCN⁻ anions and coordinate to the cobalt center, forming a $[Co(NH_3)_6]^{2+}$ complex (Figure 5(c)). Subsequently, the NH₃ molecules interact with four SCN⁻ anions by hydrogen bonds between H atoms of NH₃ and N atom of SCN⁻, finally forming an octahedral coordinated cobalt complex $[Co(NH_3)_6(NCS)_4]^{2-}$. The computed bond orders for four Co-N bonds are about 1.0, and the computed ΔG is -0.6 kcal·mol⁻¹ (Supporting Information, Equation S6), indicating the chemical bonding characteristics of the Co-N bonds. This slightly negative value means that NH₃ desorption is possible when increasing the temperature of the IL-NH₃ system, which is consistent with our experiments, i.e., NH₃ starts to be released from the cobalt ILs at 80°C. For comparison, we also calculated the ΔG for NH₃ adsorption by a neutral compound Co(SCN)₂ (Supporting Information, Equation S7), which shows a lower capacity of 3.83 molNH₃·molCo(SCN)₂⁻¹ than the cobalt ILs. The overall reaction is strongly exothermic with a computed ΔG of -16 kcal·mol⁻¹ per NH₃ (Supporting Information, Figure S8), implying that it is impossible for NH₃ desorption from the metal salt Co(SCN)₂. In addition, an optimized structure for [Co(NCS)₄(CO₂)₄]²⁻ was obtained as shown in Figure 5(d). The shortest distance between CO₂ and Co(NCS)₄²⁻ based on WBO analysis. The cobalt ILs have about 3 to 4 times higher CO₂ capacity than that of the conventional ILs due to four absorption sites (i.e. SCN⁻) in the cobalt ILs while only one in the conventional ILs. This is in consistence with the experimental results.

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Figure 5. Optimized structures of (a) SCN⁻ with CO₂, (b) SCN⁻ with NH₃, (c)[Co(NH₃)₆(NCS)₄]²⁻, and (d)[Co(NCS)₄(CO₂)₄]²⁻. The selected distances are given in angstrom, Å. Color legend: S

yellow, N blue, C black, O red and H white

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The experimental and simulated IR spectra were also further compared to examine NH₃ absorption mechanism by the cobalt ILs (Figure 6). As shown in Figure 6(a), four newly appeared bands in the experimental IR spectrum of [Bmim]₂[Co(NCS)₄] after NH₃ absorption were observed, i.e. bands A1 (~1200 cm⁻¹), A2 (~1600 cm⁻¹), A3 (~3300 to 3500 cm⁻¹) and B (~2800 cm⁻¹). Among them, the peaks A1, A2 and A3 are essentially corresponding to vibrational modes of NH_3 as the comparison of the IR spectra of $Co(NH_3)_6^{2+}$ (Figure 6(c)) with the IR spectra of a free NH₃ molecule (Figure 6(f)), indicating that chemical absorption of NH₃ occurs in $[Bmim]_2[Co(NCS)_4]$. For example, the peaks around 1200 cm⁻¹ (A1) and 1600 cm⁻¹ (A2) are the N-H wagging mode and the H-N-H scissoring mode, respectively. The third one, A3 (~3300 to 3500 cm⁻¹), is the N-H stretching mode, including symmetric and asymmetric stretching. For free NH_3 molecules, the intensities of both modes are relative low, i.e. 2.4 and 0.009 km·mol⁻¹, for symmetric and asymmetric stretching, respectively. When coordinating with cobalt atom, these two modes become stronger with computed intensities increasing to 20 (\sim 3380 cm⁻¹) and 50 (\sim 3467 cm⁻¹) $\text{km}\cdot\text{mol}^{-1}$, respectively. The fourth peak, B (~2800 cm⁻¹), is the C–H stretching mode of the CH group in the five-membered ring of Bmim⁺ cation if we analyze the IR spectra of [Bmim][SCN]. After NH₃ absorption, SCN⁻ in $Co(SCN)_4^{2-}$ complex is replaced by NH₃ and interacts with NH₃ only though hydrogen bonds (Figure 6(a)). As a result, SCN⁻ becomes a nearly free anion. This allows the N atom of SCN⁻ to interact with CH group from the Bmim⁺ cation forming N^{...}H–C hydrogen bonds, resulting in a vibrational mode around 2800 cm⁻¹. We indeed observed a band of about 2800 cm⁻¹ in the experimental IR spectra of the conventional ILs (Figure S11). The band C, which has the highest intensity, is the C–N stretching mode of the SCN⁻ anion. The last bands D (i.e. D1, D2 and D3) belong to the Bmim⁺ cation, which include the stretching mode of the C-H group in CH₃–, CH₂– and five–membered ring. Interestingly, we found that the C-H stretching mode in Bmim⁺ cation appears around 3200 cm^{-1} , and it shifts to 2800 cm^{-1} when forming a hydrogen bond with SCN⁻ anion (Figure 6(a)).



Figure 6. Experimental IR spectra of $[Bmim]_2[Co(NCS)_4]$ after (a) and before (b) absorption of NH₃. The simulated IR spectra of $[Co(NH_3)_6]^{2+}$ (c), [Bmim][SCN] (d), free NH₃ (e), $[SCN]^-$ anion

(f), and $[Bmim]^+$ cation (g)

3.8. Comparison with other ILs

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In order to evaluate the potential of ILs for NH₃ absorption, NH₃ absorption

capacity in the cobalt ILs $[C_n mim]_2[Co(NCS)_4]$ were compared with other ILs reported in literature in Table 4. It was clearly seen that $[C_n mim]_2[Co(NCS)_4]$ not only have much higher gravimetric and molar capacity of NH₃ absorption than those of the reported ILs, but also exhibit excellent recyclability, which implies that the cobalt ILs $[C_n mim]_2[Co(NCS)_4]$ show great potentials for efficient and reversible removal of NH₃ from NH₃-containing exhausted gas.

ILs	Temperature	Pressure	NH ₃ capacity		Defense
	°C	MPa	$molNH_3 \cdot molIL^{-1}$	$gNH_3 \cdot gIL^{-1}$	Kelefences
[Emim] ₂ [Co(NCS) ₄]	30	0.10	5.99	0.198	This work
[Bmim] ₂ [Co(NCS) ₄]	30	0.10	6.03	0.180	This work
[Hmim] ₂ [Co(NCS) ₄]	30	0.10	6.09	0.166	This work
[Emim][SCN]	30	0.10	0.18	0.018	This work
[Bmim][SCN]	30	0.10	0.19	0.016	This work
[Hmim][SCN]	30	0.10	0.20	0.015	This work
[Emim][BF ₄]	25	0.11	0.18	0.016	16
[Bmim][BF ₄]	25	0.22	0.45	0.034	16
[Hmim][BF ₄]	25	0.22	0.56	0.038	16
[Omim][BF ₄]	25	0.12	0.39	0.024	16
[Emim][Tf ₂ N]	25	0.14	0.15	0.007	14
[Bmim][PF ₆]	25	0.17	0.54	0.032	14
[EOHmim][BF ₄]	20	0.10	1.70	0.135	26

Table 4. Comparison of NH₃ capacity with other reported ILs

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[Choline][Tf ₂ N]	20	0.10	1.86	0.082	26
[TMG][BF ₄]	20	0.10	1.08	0.046	47
[Bim][Tf ₂ N]	40	0.10	2.69	0.113	18
[Bmim][Tf ₂ N]	40	0.10	0.28	0.011	18
[HOOC(CH ₂) ₃ mim][NTf ₂]	40	0.10	1.54	0.058	18

4. Conclusions

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In summary, a new strategy to design MILs with highly efficient and reversible absorption of NH₃ through the cooperative interactions between the metal coordination ions and NH₃ has been proposed. By screening the suitable metal centers and ligands, the cobalt ILs $[C_nmim]_2[Co(NCS)_4]$ were synthesized for NH₃ absorption. The results demonstrated that $[C_nmim]_2[Co(NCS)_4]$ not only exhibit superior recyclability, but also show very high NH₃ capacity up to 6.09 molNH₃·molIL⁻¹, which is much higher than all reported ILs to date, and is over 30 times higher than the conventional ILs $[C_nmim][SCN]$. Spectroscopic investigations and simulation calculations confirmed that significant improvement in NH₃ capacity and regeneration performance of the cobalt ILs is attributed to the moderate Lewis acid-base and cooperative hydrogen bond interactions between the metal centers-ligands and NH₃. We believe that the cobalt ILs will be potential candidates for efficient purification and recyle of NH₃ from industrial NH₃-containing gases.

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Notes and references

[‡] The optimized structures of ILs with NH₃ and CO₂, the recycle of cobalt ILs with saturated water, the experimental IR and NMR spectra, the simulated IR spectra as well as Cartesian coordinates were shown in the Supporting information.

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Table of Contents



Cobalt ionic liquids with highly efficient and reversible absorption of NH₃ through Lewis acid-base and hydrogen bond interactions were designed.