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Absorption of Flue-Gas Components by Ionic Liquids

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Gas separation by ionic liquids (ILs) is a promising new research field with several potential applications of industrial interest. Thus cleaning of industrial off gases seems to be attractive by use of ILs and Supported Ionic Liquid Phase (SILP) materials. The potential of selected ILs for absorption of NO_x, CO₂ and SO₂ are demonstrated and the possible mechanism of absorption described on the molecular level. Special focus regards the interaction of the ILs with water vapor, which is an important feature in envisaged application of flue gas cleaning in power plants, waste incineration plants, cement and glass factories as well as on board ships.

Introduction

A major concern in relation to atmospheric pollution and climate changes is emission of acidic gases such as NO_x, SO_x and CO_x from combustion of fossil fuels in, e.g. power plants. Accordingly, these gases have to be effectively removed from flue gases. Presently this is mainly achieved by relatively energy intensive and resource demanding technologies via selective catalytic reduction (SCR) of NO_x with ammonia, SO₂ wet-scrubbing by lime obtaining gypsum and CO₂ wet-scrubbing with organic amines obtaining carbamates. The latter leads to particular concern about, e.g. intensive energy requirements for desorption, corrosion of steel pipes and pumps, CO₂ absorption capacity and thermal decomposition of the amine.

In this work we demonstrate how ionic liquids (ILs) can be applied as selective, high-capacity absorbents of environmentally problematic flue gases like, e.g. SO₂, NO/NO₂ and CO₂. Reversible absorption has been obtained for several different ILs at different temperatures and flue gas compositions. The structures of ILs are well-ordered even in the liquid state with regular cavities which can host selected solute species depending on the IL ion composition. This makes the materials promising for selective, reversible absorption of gaseous pollutants in, e.g. power plant flue gases and other industrial off-gases (1,2). Furthermore, different porous, high surface area carriers like mesoporous silica and titania have been applied as supports for the ionic liquids to obtain Supported Ionic Liquid-Phase (SILP) absorber materials, Figure 1. These materials benefit from low mass transport resistance of the often highly viscous ILs by the distribution of the liquid as a thin film (or small droplets) on the surface of highly porous carrier materials which enable fast absorption/desorption rates of the particular gas exposed to the SILP absorber (3).

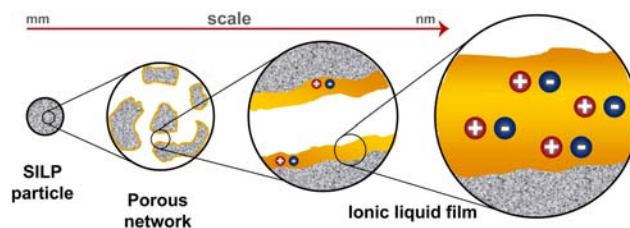


Figure 1. Principle of SILP materials.

Experimental

Materials

Synthesis of 1-butyl-3-methylimidazolium nitrate [BMIm]NO₃. 1-butyl-3-methylimidazolium nitrate was prepared using commercially available [BMIm]Cl (Fluka, >99%). The anion was exchanged by dissolving the [BMIm]Cl in water and adding a solution of silver nitrate in water to precipitate AgCl. Just below equivalent amounts of AgNO₃ was used to avoid silver pollution in the IL. After mixing, the solution was left overnight to ensure complete precipitation. The solution was then filtered (repeated 6 times) after gently heating to aid clotting of the precipitate. Finally, the water was removed under reduced pressure (10 mbar, 40°C) followed by heating under high vacuum resulting in clear viscous [BMIm]NO₃. The water content of the IL was measured by Karl Fisher titration to be 1.1%.

Synthesis of 1,1,3,3-tetramethylguanidinium chloride [TMGH]Cl. The 1,1,3,3-tetramethylguanidinium chloride was prepared by direct neutralization of an ethanolic (99.9%, Aldrich) solution of TMG (99%, Aldrich) with hydrochloric acid (37%, Aldrich) (4). To an ice-bath cooled stirred solution of TMG (11.5 g, 0.10 mol) in ethanol (100 mL) concentrated hydrochloric acid (0.10 mol) was carefully added. Caution: neutralization of base with a strong acid is highly exothermic. After continuous stirring (25 °C, 24 h), the solvent was removed under reduced pressure with heating at 70°C followed by heating under high vacuum. The product was recrystallized in ethanol.

Synthesis of tetrahexylammonium prolinatate [N6666][Pro]. 40 wt% aqueous solution of tetrahexylammonium hydroxide, [N6666]OH (13.92 g, 15 mmol, Sigma-Aldrich) and L-proline (1.89 g, 16 mmol, Sigma-Aldrich) was mixed and the solution stirred overnight at room temperature to ensure full deprotonation of the amino acid. Most of the water was removed under reduced pressure (10 mbar, 40 °C), and excess amino acid removed from the product by filtration after addition of cold acetonitrile (10 mL) and immersion into an ice bath for 1 h. Finally, the solvent was evaporated under reduced pressure to obtain the IL. The NMR and FT-IR spectra confirmed the identity of the ionic liquid. The purity of the IL was estimated by integration of visible impurities in the ¹H NMR spectrum. Yield > 99 %. Purity > 99 mol %.

Preparation of SILP absorbers. The SILP absorbers were prepared using fractionated (180-355 μm) silica, anatase and carbon support materials. The pore volume and specific area of the support materials were determined from nitrogen physisorption by BET

measurements on a Micromeritics ASAP 2020 pore analyser after out gassing the samples in vacuum at 200 °C prior to measurement (see Table I).

TABLE I. Characteristics of the SILP support materials.

Support material	Type	Surface Area (m ² /g)	Pore Volume (cm ³ /g)
Carbon	Black Pearl 1400 (Cabot)	580	0.71
Anatase	ST 31119 (Saint-Gobain)	150	0.38
Silica	SS 611138 (Saint-Gobain)	251	0.93
Silica	Gel-90 (Fluka)	257	0.93

NO SILP absorbers were prepared by suspending support material in an excess of solvent (methanol for anatase and silica, dichloromethane for carbon) and then adding [BMIm]NO₃ corresponding to a pore volume filling degree of 25-30% to the mixture. After stirring the solvent was removed using a rotary evaporator. The evaporation was performed at slightly reduced pressure and ambient temperature in order to give the best possible distribution of IL on the surface of the support. In the case of silica (Saint-Gobain), two type of SILP absorbers were prepared; one with the fractioned silica as is and one with fractioned silica that had been calcined at 500 °C for 20 h and cooled to room temperature in a desiccator.

SO₂ SILP-absorbers were made in a similar way as the NO SILP absorbers by wet impregnation by an ethanolic solution of [TMGH]Cl on SiO₂ (Fluka). In the investigation only the absorption optimized SILP of 20 wt% was used.

Gas absorption methods

NO absorption: NO removal with SILP-absorbers was performed using a fixed-bed reactor system with about 3 g SILP absorber as outlined previously (5). A simulated flue gas containing 0.2 vol% NO (AGA) and 16 vol% O₂ in N₂ with and without ~2 vol% water was adjusted by Bronkhorst mass-flow controllers to a total flow of 50 ml/min and passed through the reactor interacting with all of the material. The reaction was followed by gas phase UV-Vis (Lambda 11 UV/Vis spectrophotometer) with a gas cuvette of path length 10 cm downstream of the reactor. The NO removal could be followed by integration of the characteristic lines from NO (227 nm) in the spectrum and comparison to the spectrum of the bypass flow. NO₂ and N₂O₅ were observable as a broad, slightly asymmetrical band at approximately 218 nm (NO₂) and a broad, symmetrical band centered at around 191 nm (N₂O₅). The amounts of these gases could not be quantified reliably by the same method.

SO₂ absorption: The measurements on the SO₂ SILP-absorbers were performed in a similar setup as used for the NO absorption studies (see above) using about 4 g of absorber and a dry or wet gas flow of 100 ml/min 3% SO₂ in N₂ (Air Liquide). The SO₂ concentration in the carrier stream was determined by UV-Vis (JACS V570 UV/Vis/NIR spectrophotometer).

CO₂ absorption: Absorption of CO₂ in different amino acid-based ILs was performed at 1 bar CO₂ at room temperature with 1.0-1.2 g ILs in bubble reactors by monitoring the mass increase on an analytic balance (Sartorius CPA324S, accuracy ±0.0001 g) at regular intervals.

Thermal methods

Enthalpy of fusion and heat capacity: Enthalpy of fusion (ΔH_{fus}) and heat capacity (C_p) were measured for SO₂ absorption with a DSC 111 SETARAM calorimeter. The temperature of the thermostat was measured by the resistance of a suitable Pt resistor, which was calibrated by the melting points of standards. All around the reference and the sample cylindrical cells were placed thermopiles of Tian-Calvet type, which consists of many thermocouples connected in series. At a given temperature, the voltage difference between the two thermopiles is proportional to the differential heat flux through the walls of the reference and the sample cells. By recording the thermogram the enthalpy of reaction or transformation can be measured. For an ideal instrument of perfect thermal symmetry, the differential heat flux is zero under constant temperature or dynamic changing temperature conditions. Asymmetries may arise from several effects: Static effects due to the ineluctable asymmetry in the cells and sensors and their location, which translate into a stationary flux recorded at any given temperature. The data processing must take the corrections of asymmetric heat flows into account.

C_p was measured by the step method which consists in programming the temperature and measuring differential heat fluxes between reference and sample cells. At each step the integration of the differential heat flux divided by the temperature step gives the value of C_p . First a blank experiment using empty sample containers was performed. Then, at the same temperature and time conditions a known mass of sample was added in the sample container and a similar run achieved. Calibration with a standard NBS-Al₂O₃ sample finished the measurement. An inaccuracy generally less than 5% is expected for enthalpy and C_p measurements.

Heat of gas absorption: The integral or partial enthalpies of dissolution of gases in liquids or solids (ΔH_{diss}) can be measured by direct reaction calorimetry. In an ambient temperature Tian-Calvet calorimeter, the sorbent was placed in a special glass cell containing a device for flowing a gas or a mixture of gases. The applied calorimeter was of classical design with thermopiles as described above, but including hundreds of thermocouples. The heat flux sensitive volume was 14 cm³. The calorimeter with special characteristics of high sensibility (70 $\mu\text{W}/\mu\text{V}$) and very high stability (less than $\pm 20\mu\text{W}$ over several days) was used in isothermal mode up to 80 °C in a temperature controlled room at 19.5 ± 0.1 °C. The gas flow was controlled by Brooks mass-flow meters calibrated for SO₂ and Ar, respectively, at a sufficiently low flow not disturbing the heat flow of the calorimeter.

Results and Discussion

NO absorption

Recently, it has been found that NO can be absorbed and oxidized to nitric acid (HNO₃) in several ILs according to equation [1] (6,7).



Water is needed in the reaction but it is also possible that water can inhibit the uptake of NO. It is most probable that the anion of the IL activates the otherwise unreactive NO

molecule by nucleophilic attack. Extensive hydrogen bonding is expected to take place when water is dissolved in the IL, possibly weakening the basicity and the nucleophilic strength of the anion. The identity of the cation of the IL does not seem to play any significant role for the rate nor the capacity (6). In analogous measurements with SILP materials containing other IL anions (results not shown) a different initial rate of uptake was found.

The initial absorption capacity (interpreted as the UV-silent time) of a SILP material consisting of [BMIm]NO₃ on anatase was determined at water:NO molar ratios of 1:1 and 10:1 in the gas corresponding to 2:1 and 20:1 in stoichiometric terms according to equation [1] (Figure 2). The initial uptake appeared to be largely independent of the water concentration, and no apparent inhibition was found when increasing the water content of the simulated flue gas. At steady state a small but significant decrease in NO₂ content in the effluent flue gas was observed. This is likely caused by a larger fraction of the NO₂ molecules reacting with water according to equation 2.

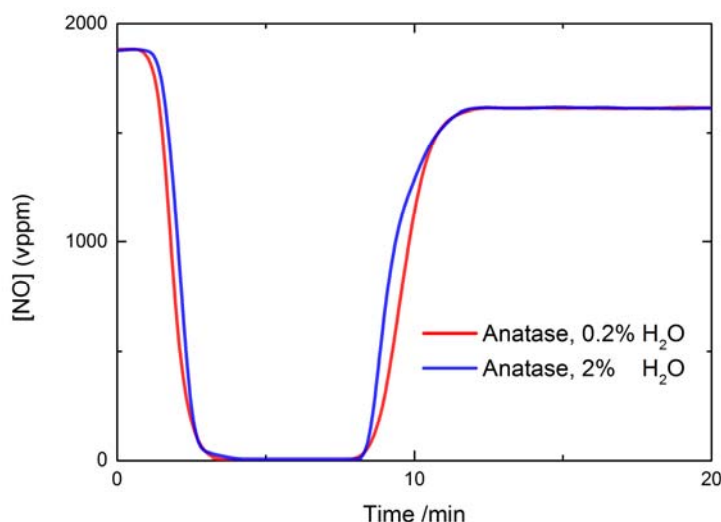
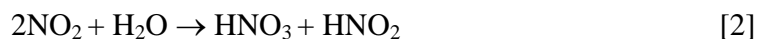


Figure 2. Concentration of NO measured downstream of the absorber for an anatase SILP with a water:NO molar ratio of 1:1 (0.2 % water) and 10:1 (2 % water).

The absorption reaction was also investigated with lower than stoichiometric amounts of water and examples of resulting spectra after breakthrough are shown in Figure 3 for a carbon and a (uncalcined) silica based SILP, respectively. The broad absorption band seen in Figure 3 is interpreted as N₂O₅. It is usually observed in the absorption spectra when the water content of the flue gas is low. The amount of N₂O₅ increased significantly when applying more hydrophobic supports (e.g. carbon) for the SILP absorber. The formation of N₂O₅ under dry conditions is suggested to be facilitated by ionization of N₂O₄ to NO₂⁺ and NO₂⁻ in the IL (6). The formed NO₂⁺ can undergo further reaction with NO₃⁻ from the IL to form N₂O₅ observed in the gas phase downstream of the absorber. When water is present both the N₂O₄ and the N₂O₅ dissolved in the IL reacts with water, leading to formation of HNO₃ which accumulates in the IL due to the formation of strong symmetric hydrogen bonds with the nitrate anion.

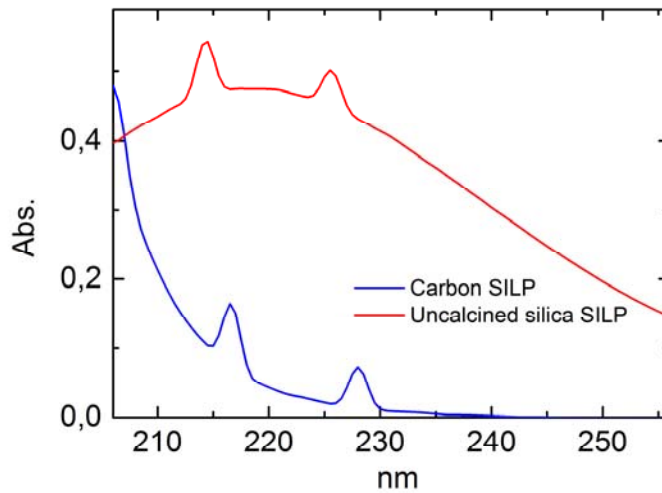


Figure 3. Post-breakthrough spectral data at sub-stoichiometric amounts of water, for two different SILP formulations.

SO₂ absorption

Figure 4 shows the results of the absorption measurements of 0.15 % of SO₂ in dry N₂ and with 2 % water vapour at 30 °C for a SiO₂ based SILP absorber with 20 wt% [TMGH]Cl. The figure shows the amount of SO₂ (mmol) detected in the gas stream after the absorber as a function of time. In the experiment the gas stream was initially bypassing the absorber and directed to the detector and after 10 min the gas flow was led to the reactor with the absorber material. From Figure 4 it is seen that the concentration of SO₂ in the gas stream dramatically drops after the gas flow was shifted from the bypass to the reactor with the absorbent. It is also seen that when the saturation of the investigated material with SO₂ is completed, the concentration of SO₂ in the outlet gas began to increase. After ca. 80 min of the reaction the concentration of SO₂ in the outlet gas was identical to the concentration of SO₂ in the inlet gas.

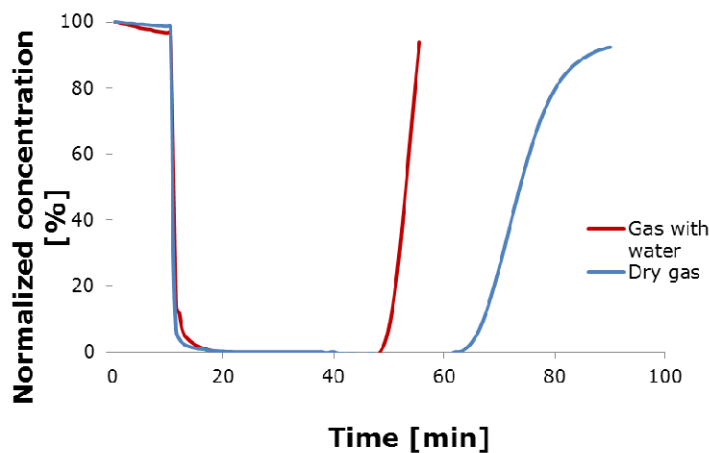


Figure 4. SO₂-absorption by 20 wt% [TMGH]Cl-SiO₂ SILP absorber in dry 0.15 % SO₂/N₂ and this gas saturated with water (3 %) until breakthrough.

The total absorption capacity for SO₂ (1500 ppm in N₂) for the 20 wt% [TMGH]Cl-SiO₂ SILP absorber at the given conditions is determined by integration of the area of absorption within the curve from 10 to ca. 80 min to be 0.05 mole fraction SO₂ in the IL for the dry gas and reduced by ca. 35% in the wet gas. The absorber material was tested by absorption and desorption of SO₂ up to 10 times in the dry gas without any significant changes in the absorption capacity as shown in our previous work (5).

Based on a X-ray investigation of crystals obtained of the SO₂ adduct [TMGH]Cl·SO₂, we previously suggested strong interaction between Lewis basic chloride ions and the Lewis acidic SO₂ molecules to account for the high absorption affinity of the salt (4). With water present in the gas the capacity is significantly reduced probably due to competition between water molecules and SO₂ regarding coordination to Cl⁻. This scenario will be further elucidated by ongoing Raman spectroscopic investigations. However, thermal investigations allowed providing insight about the energy of these interactions in dry and wet gases.

Thermal investigations of SO₂ and H₂O absorption

The DSC investigations were performed on samples of 60-80 mg of [TMGH]Cl loaded in a dry box into aluminium capsules and sealed airtight by pressing an aluminium lid into the capsule using a Ni-joint. The thermogram (DTA) was run in the range 26-225 °C at a rate of 1 °C/min. The thermogram exhibited one endothermic peak corresponding to the fusion of [TMGH]Cl at 205 °C in good accordance with the previously reported value of 208-209 °C (4).

The heat of fusion (ΔH_{fus}) of [TMGH]Cl was found to be 22.5 kJ/mol. There is no value in the literature to compare with as far as we know. The measured heat capacities (C_p) varied in the range 200-300 J/mol·K for the solid state, expressed by the polynomial $191 + 0.645 \cdot T$ in the temperature range 26-176 °C, and is equal to 420 J/mol·K within the experimental error for the liquid state in the short interval 206-225 °C.

In Figure 5 the thermograms obtained on [TMGH]Cl at 25 °C in the calorimeter under a flow of dry SO₂ gas and humid gas (2.3% H₂O in SO₂) at 1 bar total pressure are shown. The absorption of dry SO₂ gas lead to a strong exothermic effect, which by integration after calibration by heat pulses from an electrical resistance in contact with the experimental cell, gives a value of 90.35 kJ/mol for the heat of absorption of [TMGH]Cl. By weighing of the solid sample after the experiment the mole ratio of SO₂:[TMGH]Cl in the solid in the cell was found to be 1.15. These values were found to be 74.66 kJ/mol and 1.19 at 50 °C and 9.62 kJ/mol and 0.40 at 84 °C, respectively, indicating an increasingly weaker bonding of SO₂ by increasing temperature.

The absorption of humid SO₂ gas in [TMGH]Cl at 25 °C leads to an exothermic peak as well, but with a heat of absorption of 145.73 kJ/mol. The kinetics of the absorption process was obviously different for the two experiments being very slow in the humid gas only obtaining equilibrium after several days, while the dry gas absorption process was much faster taking only a few hours to reach equilibrium, as realized by blow up of the tail end of the thermograms (not shown). A marked difference was that the final product after humid gas exposure was a liquid, while it was a solid up to around 85 °C in dry gas

where it starts to melt incongruently under 1 bar dry SO₂. This solid is presumably the adduct compound TMGH]Cl·SO₂, which structure has been described recently (4).

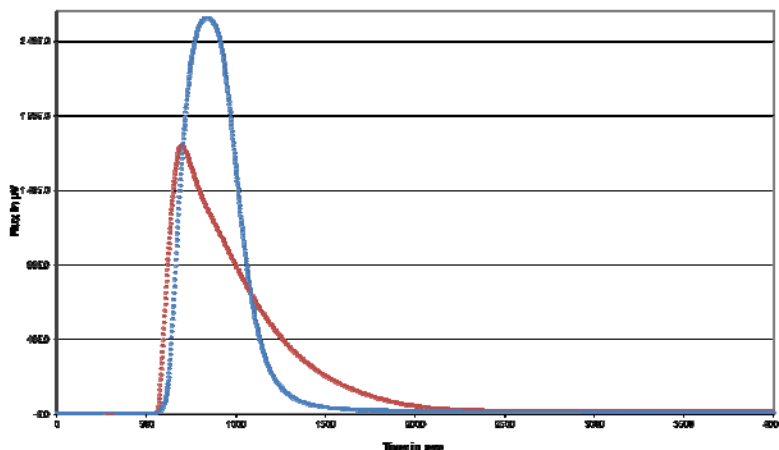


Figure 5. Thermograms (selected time period) of 1 mmol [TMGH]Cl in dry SO₂ (blue) and in humid SO₂ with 2.3 % H₂O vapor (red) at 25 °C with gas flow of 5.0 ml/min.

The absorption process in the humid gas comprised two components: A fast exothermic coordination of SO₂ to the solid TMGH]Cl followed by a slower uptake and less exothermic absorption of H₂O eventually leading to fusion of the mixture. The quantification of the equilibrium mole ratio SO₂:[TMGH]Cl in the humid gas at equilibrium is in progress. Desorption by a flow of dry Ar through the cell at 25-50 °C is a slow process leading to almost the same enthalpy as for the absorption, but slightly lower indicating that it was difficult to completely remove the absorbed components. However, successive absorption of SO₂ appeared completely reversible in this temperature range. From previous measurements on SILP absorbers (3) it is obvious that fast and reversible desorption can be performed by raising the temperature to 120 °C in a flow of, e.g. N₂ or air.

In a separate experiment at 25 °C with a flow of Ar and 2.3 % H₂O vapour, again a rather fast exothermic absorption of water by [TMGH]Cl was observed followed by a very slow further absorption of water reaching equilibrium only after several days. Again the solid was transformed to a liquid. Here the weight increase corresponded to a molar ratio H₂O:[TMGH]Cl of 4.42 and a heat of absorption of 289 kJ/mol [TMGH]Cl or 65.3 kJ/mol H₂O. This latter value is significantly higher than the heat of vaporization of water of 43.9 kJ/mol also at 25 °C. This indicates a much stronger interaction of the H₂O molecules with the ions in the formed IL, than in pure water at the same conditions. Further progress on the thermal measurements is expected in the near future.

CO₂ absorption

Previous results from our group for CO₂ absorption by amino acid-based ILs show a super-stoichiometric uptake of CO₂ (8). The effect of water on the ILs ability to take up

water is explored here. Water content seems to play an important role for CO₂ absorption by amino acid-based ILs. Not only does it lower the ILs viscosity, but it also seems to have a large positive effect on the CO₂ absorption stoichiometry and -rate. This can be seen for the IL [N6666][Pro] in Table II and Figure 6.

TABLE II. Effect of water on CO₂ absorption capacity in neat [N6666][Pro] IL at room temperature.

Entry	Ionic liquid	Water content (qualitative assessment)	CO ₂ absorption stoichiometry (mol CO ₂ /mol IL)
1	[N6666][Pro]	Wet ^a	0.71
2	[N6666][Pro]	Dried ^b	0.38
3	[N6666][Pro]	Very dry ^c	0.93

^a Dried at 15 mbar for 1 h. Probably 5-10 % water. ^b Dried at 1 mbar for 24 h. Probably 1-2 % water. ^c Dried at 1 mbar for 24 h followed by three freeze-pump-thaw cycles. Water content measured to be < 0.01 % by Karl-Fischer.

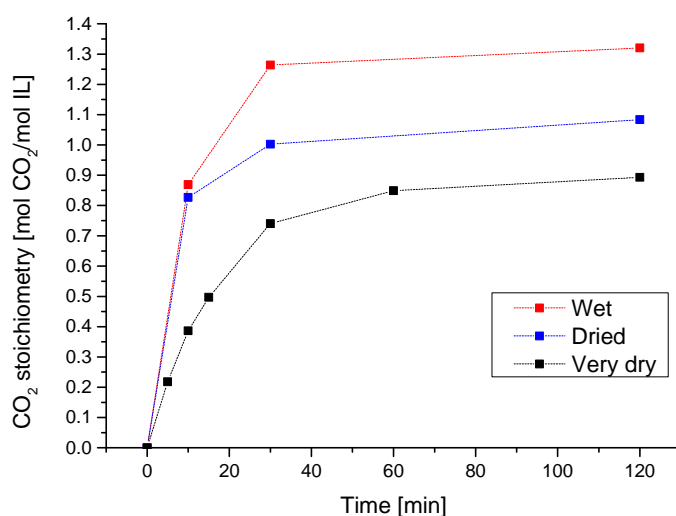


Figure 6. CO₂ absorption capacity in [N6666][Pro] at room temperature as a function of time with varying degrees of IL dryness (see Table II).

In the experiment, all mass at time zero was assumed to be IL and the absorption stoichiometries have been calculated accordingly, despite that a significant percentage of the wet sample was water. Surprisingly, a higher water content was not only associated with a higher CO₂ uptake stoichiometry, but seems to be a prerequisite for the previously reported super stoichiometric CO₂ uptake (8). The solubility of CO₂ in pure water at 25 °C and 1 atm is only 6·10⁻⁴ mol per mol of H₂O (9). Hence, this low value cannot account for the added CO₂ absorption, but the water content in the IL is most likely responsible for the super stoichiometric CO₂ uptake.

CO₂ absorption in the samples was measured by mass increase, but it can be hard to correct for a possible loss of weight from evaporation of water. Therefore, an experiment was devised in which the CO₂ absorption of the very dry sample was compared to that of a sample absorbing from a gas stream that had been pre-saturated with water by passing the gas through a wash bottle with water at room temperature. Absorption from both wet CO₂ and wet Ar gas was followed, and it is assumed that the water content in the gas streams were identical. This can be seen from Figure 7. The sample in the wet Ar stream

did not - strictly speaking - take up CO₂, but as “stoichiometry” scales linearly with weight it allowed directly comparison of the samples.

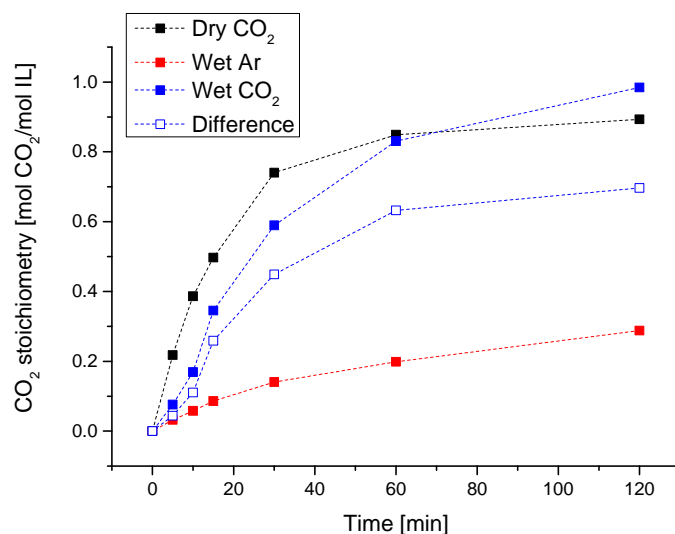


Figure 7. Uptake of CO₂ by dry [N6666][Pro] at room temperature during absorption in dry CO₂ (black), in wet Ar (red) and in wet CO₂ (blue, full), as well as in wet CO₂ corrected for mass increase in wet Ar (blue, open).

The mass of the sample in wet CO₂ did not increase more rapidly than the sample in dry CO₂. This is in agreement with experiments performed with 1,1,3,3-tetramethylguanidinium imidazolate [TMGH][Im], where presence of water slowed down the CO₂ absorption (10). A first impulse would be that the IL at first is “busy” taking up water, and it only gains absorption momentum later, which is in agreement with a minimum amount of water being needed for rapid uptake of CO₂.



Figure 8. Absorption stages in dry [N6666][Pro]. The IL is initially transparent (left) but a turbid phase appeared during absorption (right).

A possible explanation for the difference in absorption stoichiometry and rate in the presence of pre-absorbed water (Table II and Figure 7), is possibly that water facilitate a different mechanism for uptake of CO₂ that is not available in a dry gas stream. This is supported by the qualitative assessment of the ILs upon CO₂ absorption. During absorption, a turbid phase appeared in the dried and very dry samples after absorbing 1.00 and 0.38 equivalents, respectively (see Figure 8). This turbid phase did not appear

during absorption in the wet sample. This suggests that pre-absorbed water has a highly positive influence on CO₂ absorption in amino acid-based ILs. For some reason, concerted absorption of water and CO₂ did not see this positive effect – possible because water was not absorbed sufficiently fast.

Conclusions

The presented results demonstrate that NO/NO₂, SO₂ and CO₂ can be absorbed by ILs through different mechanisms of absorption. Furthermore, impregnation of porous solids to make Supported Ionic Liquid-Phase (SILP) absorbers leads to solid materials with good absorption/desorption dynamics. However, water plays a significant role for the absorption processes and the absorption capacities regarding the different gases and the investigated ILs.

Unlike separation of other acidic gases (e.g. SO₂ and CO₂) using ILs, NO absorption and oxidation in IL-based materials is less dependent on the nature of the anion. It is also less affected by the presence of large amounts of water in the gas flow. Water is necessary to provide the final product - nitric acid - but the reaction can also proceed under relatively dry conditions. In this case, the products are more dominated by the anhydrous oxidation products N₂O₄ and N₂O₅. The observation that a large excess of water is not detrimental to the removal of NO is a big advantage for deNO_x applications, since most flue gases contain large quantities of water. Furthermore, the hydrated conditions might hinder or slow down possible accumulation and poisoning of the NO absorbers by other acidic gases. Regarding absorption of SO₂ and CO₂ initially the presence of water is similarly not a drawback. It may even enhance the kinetics of absorption until saturation, but further uptake of water may lead to increasingly substitution of the absorbed molecules, thus decreasing the overall capacity for the flue-gas absorption.

The absorption/desorption process may be performed by SILP materials shaped in honey comb structures as the traditional SCR deNO_x catalyst used in power plants today, leading to optimized gas diffusion and low pressure drop of the passing flue gas. Installed as a traditional rotating heat exchanger it will facilitate desorption by elevation of the temperature in a smaller side channel and make it possible to desorb the gases in concentrated form.

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