Tuning ionic liquids for high gas solubility and reversible gas sorption

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Abstract

New 1,1,3,3-tetramethylguanidinium-based ionic liquids have been synthesized and their ability to reversibly absorb gaseous sulfur dioxide and ammonia investigated. It was found that up to 2 moles of gas at 1 bar could be absorbed per mole of ionic liquid at room temperature and almost completely desorbed by heating or lowering of the pressure. No change in absorbing capacity of the ionic liquids was observed after several cycles. The absorption of SO_2 in the ionic liquids is an exothermic process and standard enthalpy of solution was found to be in the range -21 to $-37\,kJ\,mol^{-1}$, indicating a moderate association between gas and liquid, which also could be confirmed by Raman and UV–vis spectroscopy on the gas-saturated (1 bar) ionic liquids. Knowledge of gas solubilities and the reversible gas absorption capacity of ionic liquids are believed to have importance for their possible application as reaction media for, e.g. catalytic processes involving gaseous reactants, and as absorbents in gas separation processes.

1. Introduction

Solubility of gases in ionic liquids (ILs) [1–3] is an important parameter regarding the possible application of ionic liquids as solvents for reactions involving gaseous reactants and products, as membranes for gas separations, as media for gas storage and as reversible absorbents for gases where the present paper deals with the latter issue.

Ionic liquids have been demonstrated to be excellent solvents for many reactions involving gaseous reactants entering the IL solution, including hydrogenation, hydroformylation and oxidation [4–8] despite very low IL solubility of H_2, CO and O_2 gases near ambient conditions (gas mole fraction solubilities are of the order of 10^{-4} [9–11]). Low IL gas solubility is, however, compensated by fast gas diffusion particularly for reactions involving hydrogen gas [12], while gas solubility might be the rate determining step for other IL reactions due to mass transfer limitations. However, the large number of ILs already available or new ones easy to synthesize facilitates the choice of ionic liquid with task-specific properties regarding the solubility of a particular gas to be reacted or separated from other gases in a mixture. In some cases the IL may interact with a gaseous compound through strong intermolecular associations or even regular bonding. Example of this is the use of imidazolium-based ILs (i.e. [RMIM]X) as storage media for hazardous and highly reactive gaseous AsH_3 or PH_3 (X = Cu_2Cl_3) and BF_3 (X = BF_4) [13,14], and the irreversible bonding of sulfur containing compounds by amines [15] which easily could be accomplished in a proper chosen IL.

The subject of the present paper is to study the absorption/desorption of various gases in ionic liquids giving rise to intermolecular interactions of intermediate strength, allowing reversible absorption of the particular gas, i.e. by moderate change of temperature or pressure. Such absorbents are interesting for alternative technologies regarding, e.g. capture of CO_2 from combustion of fossil fuels [16] and SO_2 in different types of off-gases [15–17]. Previously it was shown [17] that the ionic liquid [TMGH]L (1,1,3,3-tetramethylguanidinium lactate) could absorb approx. 1 mole SO_2 per mole IL at 1 bar SO_2 and 40 °C. Additionally, almost simultaneously it was later reported by Maginn and Brennecke [16] that [HMIM]Tf$_2$N (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) and [HMPY]Tf$_2$N (1-hexyl-

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3-methylpyridinium bis(trifluoromethylsulfonyl)imide) also could absorb around 1 mole of SO_2 per mole IL at 1 bar SO_2 and 25 °C, and by us [18] that TMG- and BMIM-based (1-butyl-3-methylimidazolium) ionic liquids reversibly could absorb up to 1.6 mole SO_2 per mole IL at 20 °C and 1 bar SO_2. Very recently [19] we reported initial results regarding increased SO_2 absorption by modification of substituents on the [TMGH]+ cation leading to the so far highest reported ratio of mole SO_2 absorbed/mole IL of 2. In the present paper we extent this work and apply Raman spectroscopy in order to study the interaction between the SO_2 molecule and the ionic liquid as well as we explore the absorbing capacity of the ILs for gaseous ammonia.

2. Experimental

In the study five different TMG-based ionic liquids were synthesized from TMG via the routes outlined in Scheme 1, and subsequently used for comparative gas sorption experiments with NH_3 and SO_2 gases with the common ILs [BMIM]X (X = BF_4 and Tf_2N). More details about materials and equipment used for IL syntheses and characterization and gas sorption experiments are given below.

2.1. Materials and apparatus

Lithium bis(trifluoromethylsulfonyl)imide (p.a.), sodium hydroxide (p.a.) fluoroboric acid (50 wt.% solution in water), 1,1,3,3-tetramethylguanidine (TMG, 99%), *n*-iodobutane (99%), propyl bromide (99%), propylene oxide (99%), ethanol (99%), toluene (99.8%) and methylenchloride (99.8%) were purchased from Aldrich. SO_2 gas (99.95%) and N_2 gas (99.99%) were purchased from Air Liquide, Denmark. All reagents were used as received. The ionic liquids [BMIM]BF_4 [20] and [BMIM]Tf_2N [21] were prepared by literature procedures

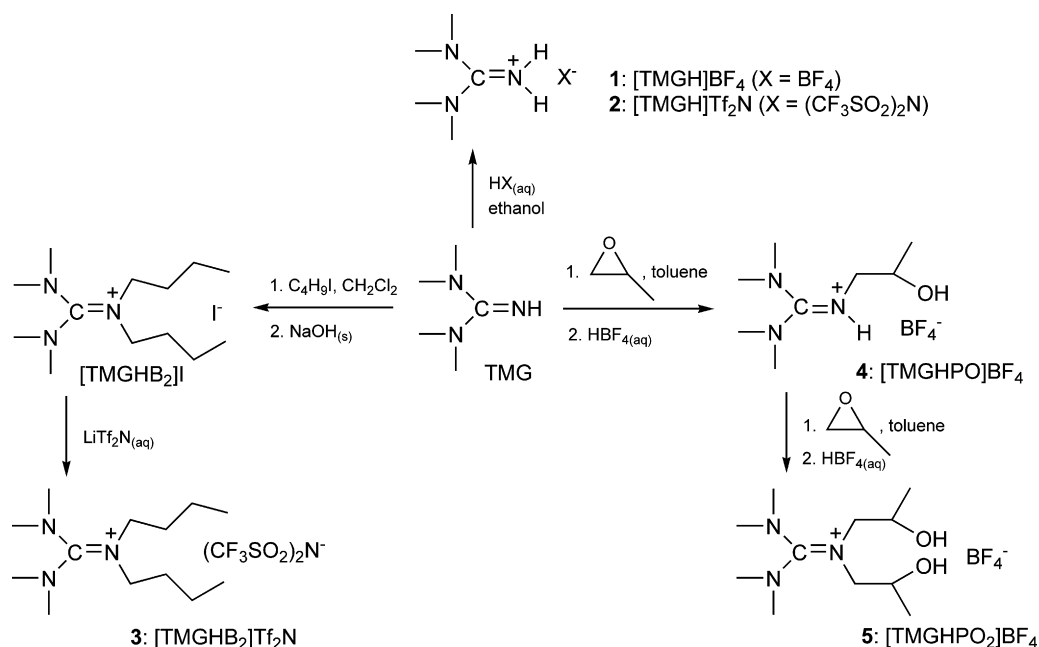and dried by heating under vacuum (0.1 mbar, 70 °C) prior to use.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM360 NMR spectrometer in $CDCl_3$ or d^6-DMSO at 25 °C and peak positions are reported relative to the solvent ($CDCl_3$: δ_H = 7.26 ppm; d^6-DMSO: δ_H = 2.50 ppm, δ_C = 40.45 ppm). Melting points (T_m) were determined by differential scanning calorimetry using a TA-2620 DSC equipped with cryostat cooling (5–20 mg samples, 5 °C min^{-1} heating and cooling rates). FT-IR spectra were recorded on a Perkin Elmer FT-IR 1710 spectrophotometer (25 °C) using KBR tablets containing a drop of liquid. FT-Raman spectra were recorded on a Bruker IF S66 FRA-106 FT-spectrometer (1064 nm NIR Nd-YAG laser, 100 mW, liquid nitrogen cooled Ge-diode detector, 25 °C) with sealed quartz ampules. UV–vis absorption spectra were recorded on a Cary 3 spectrophotometer (25 °C) with sealed quartz cuvettes (0.500 cm with 0.495 cm inset, i.e. light pathway 0.005 cm) under air or 1 bar SO_2.

2.2. Synthesis of ionic liquids

2.2.1. [TMGH]BF_4 **1** and [TMGH]Tf_2N **2**

The ionic liquids [TMGH]BF_4 and [TMGH]Tf_2N were prepared by direct neutralization of ethanolic TMG solution with aqueous fluoroboric acid (HBF$_4$) or aqueous HTf$_2$N solution, respectively (Scheme 1) [18]. The HTf$_2$N solution was prepared by cation exchange of LiTf$_2$N on Dowex® 50 W × 2 resin (hydrogen form, Aldrich).

In preparation of the ILs **1** and **2**, concentrated 50% HBF$_4$ (17.6 g, 0.10 mol) or 2.0 M HTf$_2$N (50 mL, 0.10 mol) was carefully added to a stirred solution of TMG (11.5 g, 0.10 mol) in ethanol (100 mL) while cooling the solution on an ice bath (*Caution: Neutralization of strong base with a strong acid is highly exothermic*). After continuous stirring (25 °C, 24 h) the solvent

Scheme 1. Synthetic routes for the used TMG-based ionic liquids.

was removed under reduced pressure (1 mbar) by heating to 70 °C, followed by heating under vacuum (0.1 mbar), leaving the ionic liquids behind in near quantitative yield.

[TMGH]BF$_4$ **1**: $T_m = -32$ °C; ^{1}H NMR (300 MHz, d^6-DMSO): $\delta = 2.29$ (s, 12H; CH$_3$), 5.59 ppm (s, 2H; NH$_2$); ^{13}C NMR (75.5 MHz, d^6-DMSO): $\delta = 39.55$ (N–CH$_3$), 161.48 ppm (N=C).

[TMGH]Tf$_2$N **2**: $T_m = 35$ °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 3.01$ (s, 12H; CH$_3$), 6.20 ppm (s, 2H; NH$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 39.62$ (N–CH$_3$), 122.08 (CF$_3$), 161.38 ppm (N=C).

2.2.2. [TMGHB$_2$]Tf$_2$N 3

The ionic liquid [TMGHB$_2$]Tf$_2$N were synthesized by alkylation of TMG with *n*-iodobutane (C$_4$H$_9$I) followed by anion exchange with LiTf$_2$N [18].

Initially, TMG (11.5 g, 0.1 mol) was added drop wise to a stirred solution of C$_4$H$_9$I (38.7 g, 0.21 mol) in methylenchloride (100 mL) while maintaining the temperature at 25 °C. The reaction vessel was then closed and stirred at room temperature for 24 h. Afterwards, solid NaOH (6.0 g, 0.15 mol) was added and the vessel stirred for another 24 h after closure. The obtained solution was then filtered and the solvent removed under reduced pressure (1 mbar, 70 °C) to obtain a white intermediate solid product of [TMGHB$_2$]I.

The IL **3** was subsequently obtained as a separate phase after anion exchange of an equimolar solution of [TMGHB$_2$]I (7.12 g, 0.02 mol) in 30 mL water with LiTf$_2$N (5.74 g, 0.02 mol). The separated [TMGHB$_2$]Tf$_2$N was successively washed with 3 × 5 mL water and dried under reduced pressure (1 mbar, 70 °C) followed by heating under high vacuum (0.1 mbar), to yield a colorless liquid in near quantitative yield.

[TMGHB$_2$]Tf$_2$N **3**: $T_m = -42$ °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.95$ (t, 6H; CH$_3$), 1.32 (m, 4H; CH$_2$), 1.65 (m, 4H; CH$_2$), 2.98 (s, 12H; N–CH$_3$), 3.20 ppm (m, 4H; N–CH$_2$); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 13.83$ (CH$_3$), 20.16 (CH$_2$), 29.20 (CH$_2$), 40.48 (N–CH$_3$), 49.62 (N–CH$_2$), 122.27 (CF$_3$), 161.50 ppm (N=C).

2.2.3. [TMGHPO]BF$_4$ 4

The ionic liquid **4** was prepared by allowing an equimolar amount of propylene oxide to react with TMG in a similar manner as previously reported [19,22].

Propylene oxide (7.0 mL, 0.10 mol) was drop wise added to a stirred solution of TMG (11.5 g, 0.10 mol) in toluene (100 mL) while maintaining the temperature at 25 °C. The reaction vessel was then closed and stirred at room temperature for additionally 48 h, where after concentrated 50% fluoroboric acid (17.6 g, 0.10 mol) was carefully added to the stirred solution while cooling in an ice bath. After removal of the solvent under reduced pressure with heating (1 mbar, 70 °C) and drying under high vacuum (0.1 mbar) a colorless, viscous ionic liquid was obtained.

[TMGHPO]BF$_4$ **4**: $T_m < -60$ °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.05$ (d, 3H; CH$_3$), 2.98 (s, 12H; N–CH$_3$), 3.3 (m, 1H; CH), 3.55 (d, 2H; CH$_2$), 3.85 (s broad, 1H; OH), 6.5 ppm (s broad, 1H; NH); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 18.94$ (CH$_3$), 39.76 (N–CH$_3$), 68.19 (CH$_2$), 68.56 (CH), 161.80 ppm (N=C).

2.2.4. [TMGHPO$_2$]BF$_4$ 5

[TMGHPO$_2$]BF$_4$ **5** was prepared by reaction of an additional equivalent of propylene oxide with [TMGHPO]BF$_4$ **4**, using a similar procedure as applied for the synthesis of **4** [19]. In this way a near quantitative yield of a colorless liquid was obtained, which gradually became more viscous (without solidifying) upon extensive drying.

[TMGHPO$_2$]BF$_4$ **5**: $T_m < -60$ °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 1.15$ (d, 6H; CH$_3$), 3.0 (s, 12H; N–CH$_3$), 3.4 (m, 2H; CH), 3.6 ppm (m, 4H; CH$_2$); ^{13}C NMR (75.5 MHz, d^6-DMSO): $\delta = 19.35$ (CH$_3$), 39.50 (N–CH$_3$), 68.02 (CH$_2$), 68.81 (CH), 161.87 ppm (N=C).

2.3. Gas absorption–desorption experiments

The absorption of the pure gases SO$_2$ and NH$_3$ in ionic liquids were carried out under magnetic stirring (400 rpm) at a pressure of 1 bar and at room temperature (20 °C) by passing a gas stream (50 mL min^{-1}) via a finely sintered glass frit through about 3.50 g of degassed (0.1 mbar, 2 h, 70 °C; re-pressurized with N$_2$ gas) ionic liquid loaded into individual cylindrical glass tubes (length 120 mm, inner diameter 12 mm) with gas inlet and outlet valves. The glass tube containing the IL (and stirring bar) was immersed in an insulated silicon oil bath, which was placed on a magnetic stirrer (VWR 810 digital) that allowed temperature control by a L-type thermo element. Positioning of the thermo element at the outer wall of the glass tube allowed carefully temperature control (± 0.1 °C) throughout the experiments. During gas absorption the mass increase of the IL phase, which allowed the gas solubility (reported as mole fraction) to be determined, was measured at regular intervals by weighing the tube on an analytical electronic balance (Mettler AE200, ± 0.001 g) after closing the gas inlet and outlet valves to retain a gas pressure of 1 bar (± 0.05 bar). To ensure that thermodynamic equilibrium was attained the weighing procedure was repeated until the mass remained constant (typically within 1 h) between consecutive measurements.

Desorption of gas from the ILs saturated with SO$_2$ (1 bar, 20 °C) were carried out by heating the tube with the gas-outlet valve open at fixed temperatures in the interval 20–140 °C (± 0.1 °C) in a step wise manner. This allowed gas solubility (reported as mole fraction) to be determined as a function of temperature. The gas content in the IL was measured gravimetrically as described for the absorption experiments above. Hence, when gas evolution ceded (typically within 0.5–1 h) at a given set-temperature indicative of complete gas desorption, the solution was weighted successively (with closed valves) until the mass remained constant at the particular temperature during several heating/weighing cycles. Subsequently, the temperature was adjusted to a new set point and the procedure repeated.

3. Results and discussion

3.1. Ionic liquid sorption studies

The synthesized TMG-based ionic liquids were examined as media for reversible sorption of the gases SO$_2$, 10% SO$_2$ in N$_2$

Table 1
Gas solubility in ILs at 1 bar and 20 °C

Ionic liquid	Mole fraction of gas in IL[a] (20 °C)				$\rho^{20°C}$ (g/cm^3)	V_m^{IL} (L/mol)	$V_{SO_2(g)}/V^{IL}$
	X_{NH_3}	X_{SO_2}	X_{SO_2} (at 0.1 bar SO$_2$)	X_{CO_2}			
[BMIM]BF$_4$	0.495	0.600[b]	(0.005[b])*		1.21[h]	0.202	184.0
[BMIM]Tf$_2$N		0.571[b]	(0.007[b])*		1.43[i]	0.293	112.5
[BMIM]PF$_6$				0.017[d]	1.36[i]	0.209	
[TMGH]BF$_4$	0.519	0.559[b]	0.060[b]		1.27	0.160	196.7
[TMGHPO]BF$_4$		0.618[c]	0.131[c]		1.27	0.206	193.6
[TMGHPO$_2$]BF$_4$	0.415	0.668[c]	0.167[c]		1.28	0.249	200.0
[TMGH]Tf$_2$N	0.539	0.541[b]	0.057[b]		1.31	0.303	96.5
[TMGHB$_2$]Tf$_2$N		0.615[b]	0.074[b]		1.34	0.380	104.3
[TMGH]lactate		0.494[e]		0.059[k]	1.07[f]	0.192	126.0
[APBIM]BF$_4$				0.333[g]			
[HMIM]Tf$_2$N		0.478[j]			1.37[l]	0.327	69.4
[HMPY]Tf$_2$N		0.522[j]					

* These unexpected small values are under reinvestigation.

[a] The error of the mole fractions are $X_{SO_2} = 0.002$ and $X_{NH_3} = 0.007$, respectively.

[b] Ref. [18].

[c] Ref. [19].

[d] Ref. [2].

[e] Ref. [17].

[f] $T = 45$ °C [23].

[g] CO$_2$ mole fraction at 22 °C, [APBIM]BF$_4$ = 1-aminopropyl-3-butylimidazolium tetrafluoroborate [24].

[h] Ref. [25].

[i] Ref. [26].

[j] $p_{SO_2} = 0.994$ bar ([HMIM]Tf$_2$N) and 0.110 bar ([HMPY]Tf$_2$N) [16].

[k] $p_{CO_2} = 4.9$ bar, $T = 35$ °C [27].

[l] Ref. [28].

and NH$_3$ after saturated with gas at 1 bar and 20 °C. In Table 1 the measured gas solubilities of the individual gases are compiled as mole fractions of dissolved gas in IL and compared to earlier reported solubility data for SO$_2$ and CO$_2$ in other ILs at related conditions.

The gas absorption capacity of IL absorbents can be significantly increased by incorporating functional groups which interacts relatively strongly with the gas during sorption. So-called task-specific ILs (TSIL) [29] like, e.g. [APBIM]BF$_4$ (1-aminopropyl-3-butylimidazolium tetrafluoroborate) substituted with an amine group, thus enable absorption of 0.5 moles CO$_2$ per mole of IL (equal to a CO$_2$ mole fraction of 0.333) via carbamate formation [24], corresponding to about a 30-fold increase in absorption capacity compared to common ILs (e.g. [BMIM]PF$_6$) where only low CO$_2$ solubility is obtained, as shown in Table 1.

In analogous manner, the prepared functionalized TMG-based ILs were found to be better absorbents for sulfur dioxide compared to imidazolium, pyridinium and none-substituted TMG-ILs used in previous studies (Table 1). Especially the functionalized ILs with alcohol-containing alkyl chains on the cation made with propylene oxide (i.e. [TMGHPO]Tf$_2$N and [TMGHPO$_2$]Tf$_2$N) gave rise to high SO$_2$ solubilities corresponding to SO$_2$ mole fractions up to 0.668 (equal to 2.01 moles SO$_2$ per mole IL or about 40 wt.%) for the double-substituted IL. Interestingly, the alcohol functionality in the anion part of the [TMGH]lactate IL did only affect SO$_2$ solubility to a minor extent compared to the cation-functionalized ILs, indicating that the cation of the TMG ILs are the component interact-

ing most significantly with the absorbed SO$_2$ probably via the electrophilic sulfur atom. This was further supported by the observation that only a slight anion effect was found for SO$_2$ solubility between the TMG ILs containing either BF$_4^-$ or Tf$_2$N$^-$ with the later being slightly lower. Moreover, the none-substituted TMG ILs was found to absorb less SO$_2$ than the analogous BMIM-based ILs but more than the more lipophilic HMIM- and HMPY-based ILs, as expected for a polar molecule like SO$_2$.

When 10% SO$_2$ gas (10 mole% in N$_2$) was absorbed at 1 bar pressure and 20 °C in the ILs possessing the highest absorption capability instead of pure sulfur dioxide gas, SO$_2$ mole fractions of 0.131 and 0.167 were obtained at equilibrium for [TMGHPO]BF$_4$ and [TMGHPO$_2$]BF$_4$, respectively. These values corresponds to an approximately tenfold decrease in absorption capacities when reducing the SO$_2$ partial pressure from 1 to 0.1 bar (as also expected from Henry's law), allowing an estimated gas:liquid molar concentration distribution ratio of SO$_2$ about 1:200 to be determined. In comparison the analogous gas:liquid molar concentration distribution ratio of pure SO$_2$ is 1:162 at equilibrium conditions at 20 °C.

Besides sulfur dioxide also ammonia was found to be readily absorbed in the examined ILs at ambient conditions (i.e. 1 bar NH$_3$, 20 °C) giving rise to solubilities corresponding to mole fractions up to 0.539 (NH$_3$ to IL ratio of 1.17) for [TMGH]Tf$_2$N. Notably, the gas solubility of the nucleophilic ammonia was in contrast to SO$_2$ gas (electrophile) lowered in presence of electron-rich alcohol substituents on the TMG IL. This established that also absorption of basic NH$_3$ in TMG-based ILs
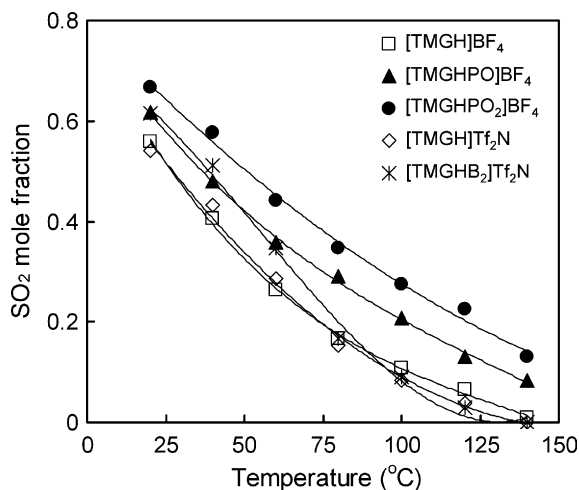
Fig. 1. SO_2 sorption profiles of TMG-based ILs shown as mole fraction of SO_2 in ionic liquids as a function of temperature.

Fig. 2. Consecutive absorption, a (at 20 °C) and desorption, d (at 140 °C) cycles of TMG-based ILs.

is predominated by cation-gas interactions, while no significant contribution to the absorption capacity can be ascribed to originate from interaction with the slightly acidic alcohol hydrogen atoms. This was supported by the fact that only a minor anion effect on absorption was observed for [TMGH]Tf_2N and [TMGH]BF_4 ILs, as in the case of SO_2 absorption.

SO$_2$ sorption in the TMG-based ILs under 1 bar pressure was also measured as a function of temperature and consecutive absorption/desorption cycles allowed the applicability of the absorbents to be evaluated for TSA (temperature swing absorption) processing. Desorption of SO_2 was carried out by heating the gas-saturated ILs at various temperatures while monitoring the weight loss periodically. In Fig. 1 the SO_2 content in the ILs (as SO_2 mole fraction) as function of desorption temperature is shown (values tabulated in Supplementary Information).

Both absorption and desorption of SO_2 gas in the examined TMG-based ILs were relatively fast, providing complete absorption in less that 1 h with pure SO_2 gas (50 ml min^{-1}, 400 rpm stirring), and in the case of the none functionalized ILs (i.e. [TMGH]BF_4, [TMGH]Tf_2N and [TMGHB$_2$]Tf_2N) essentially complete gas desorption in 0.5 h at room temperature and 1 mbar vacuum or when heated to about 140 °C. In contrast, some of the dissolved SO_2 (10–15 mole%) retained in the IL even under prolonged heating at 140 °C, clearly revealing that the presence of adjoining OH groups restrain gas absorption. Moreover, the ILs could be reused many times without any loss of absorption capability, as shown in Fig. 2 where six reversible consecutive absorption cycles are shown.

3.2. Solvent–solute interaction

Enthalpy (ΔH_{sol}) and entropy (ΔS_{sol}) of gas dissolution can be found by considering the temperature effects on gas solubilities. The enthalpy yields information about the strength of interaction between the liquid and dissolved gas, whereas the entropy indicates the level of ordering that takes place in the liquid/gas mixture. These properties can be determined from the
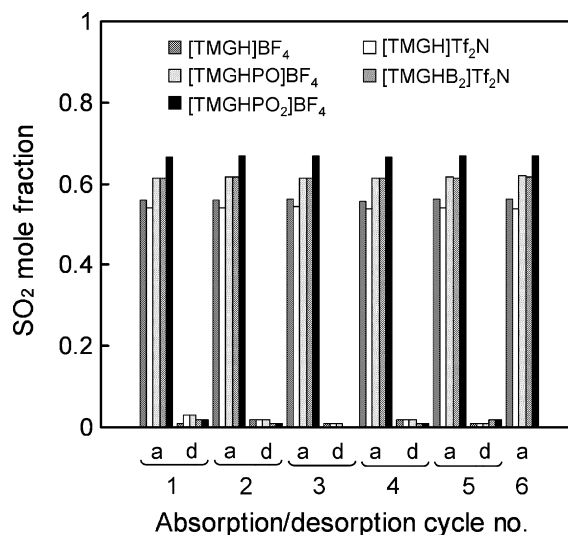
thermodynamic van't Hoff relations Eqs. (1) and (2):

$$\Delta H_{sol} = R\left(\frac{\partial \ln H_1}{\partial(1/T)}\right)_P = -R\left(\frac{\partial \ln x_1}{\partial(1/T)}\right)_P \tag{1}$$

$$\Delta S_{sol} = -R\left(\frac{\partial \ln H_1}{\partial \ln T}\right)_P = R\left(\frac{\partial \ln x_1}{\partial \ln T}\right)_P \tag{2}$$

which is valid in the Henry's law regime at infinite dissolution where the activity coefficient of the gas is independent of the amount of dissolved gas (x_1) [30]. In Table 2 the calculated values for standard enthalpy and entropy of dissolution of SO_2 in the studied ILs are shown, based on calculations derived from variations in three to five gas mole fractions measured by desorption at the highest temperatures (i.e. lowest gas solubility).

The magnitudes of the calculated enthalpies indicate a rather weak association typical of physical gas solubility and no regular bonding between the solvent and the solute SO_2 molecule. Hence, compared to the average bond energy of the S–O bonds in SO_2 of 516 kJ mol^{-1} [31] the interaction with the ILs have only about 4% of the strength of the intramolecular bonding in the SO_2 molecule increasing to around 7% in the strongest absorbing IL ([TMGHPO$_2$]BF_4). The room temperature FT-Raman spectra of two selected ILs, with and without saturation by gaseous SO_2 at 1 bar, and liquid SO_2 are compared and shown in Fig. 3.

Table 2
Standard enthalpy and entropy of SO_2 dissolution in various ILs

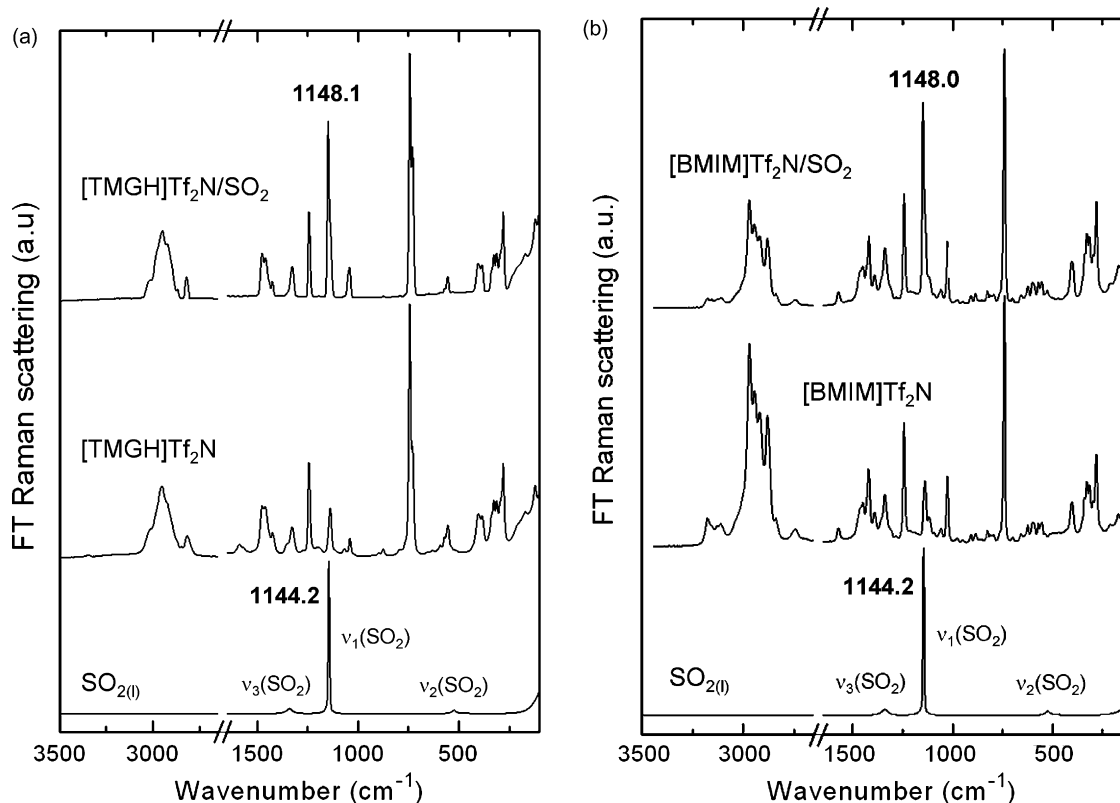| Ionic liquid	ΔH_{sol}^{θ} (kJ/mol)	ΔS_{sol}^{θ} (J/mol K)
[BMIM]BF_4	−21 ± 1	−60 ± 2
[BMIM]Tf_2N	−21 ± 1	−61 ± 2
[TMGH]BF_4	−23 ± 1	−66 ± 3
[TMGHPO]BF_4	−31 ± 1	−77 ± 3
[TMGHPO$_2$]BF_4	−37 ± 2	−91 ± 4
[TMGH]Tf_2N	−24 ± 1	−72 ± 3
[TMGHB$_2$]Tf_2N	−33 ± 1	−91 ± 4
[HMIM]Tf_2N	−20.3 ± 0.4[a]	−65 ± 1.2[a]

[a] Ref. [16].

Fig. 3. Comparison of FT-Raman spectra of liquid SO_2 with pure and SO_2 saturated ionic liquids [TMGH]Tf$_2$N (a) and [BMIM]Tf$_2$N (b).

In the Raman spectra the bands due to the IL cations, [TMGH]$^+$ and [BMIM]$^+$, are dominating at high wave numbers, i.e. above $2500\,cm^{-1}$ while the bands due to the Tf$_2$N$^-$ anion dominates below $1500\,cm^{-1}$. A more detailed assignment of the bands originating from [BMIM]Tf$_2$N can be found elsewhere [32], while the band assignment of [TMGH]Tf$_2$N will be further addressed in a forthcoming paper concerned also with the solid state of the liquids [33]. By comparison to the spectrum of liquid SO_2 no new bands appeared in the spectra of the SO_2-saturated ILs and no significant change of the frequencies of the bands originating from the pure ILs were observed. In addition only a small red shift of $\nu_1(SO_2)$ of approximately four wave numbers appeared in going from $SO_{2(l)}$ to $SO_{2(soln. IL)}$, supporting that rather weak interactions and no chemical bonding between the solvent and the solute SO_2 molecule occured in the SO_2-saturated ILs. Furthermore no significant proton shift was observed in the ^{1}H NMR spectra of the SO_2-saturated ILs [18].

When the transparent [TMGH]Tf$_2$N IL was saturated with SO_2 gas the IL obtained a yellow color. In the UV–vis absorption spectra of the pure IL and the IL saturated with SO_2 gas (Fig. 4), this is observed as a shift of the absorption band in the UV region towards lower energy (i.e. the visible region), most probably due to the $\pi \rightarrow \pi^*$ transition in the delocalized [TMGH]$^+$ entity, $[(CH_3)_2N)_2CNH_2]^+$.

This result indicate that the most important interaction is found between the cation of the IL and the SO_2 molecule thus supporting the conclusion from the previous section, that the anion of the studied ILs are of minor importance for the absorp-

tion capacity for SO_2 of the ILs. Furthermore, this suggested van der Waals type of bonding between the delocalized π bonding systems in the [TMGH]$^+$ (and possibly also in the [BMIM]$^+$) cation and dissolved SO_2, which probably also can explain the shift of the $\nu_1(SO_2)$ stretching band observed by Raman upon dissolution in the ILs since the donation of π electron density to the antibonding orbital of the S–O bonds in SO_2 will lead to a longer S–O bond and a higher wave number for the symmetric stretching frequency in SO_2.
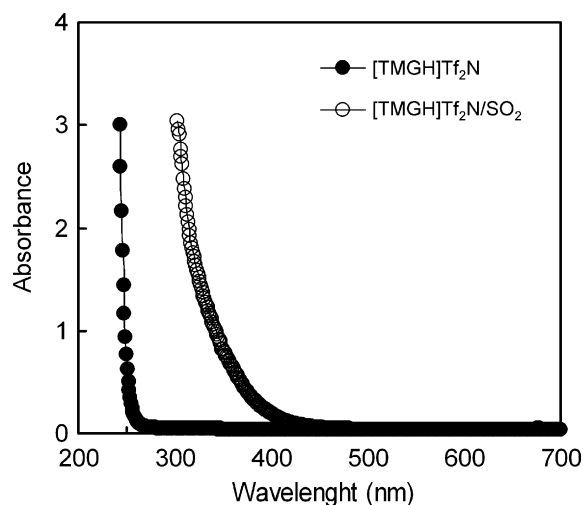

Fig. 4. UV–vis absorption spectra of pure ionic liquid [TMGH]Tf$_2$N and [TMGH]Tf$_2$N saturated with SO_2 gas at 1 bar and 25 °C.

4. Conclusions

TMG-based ionic liquids are good absorbents for both SO_2 and NH_3 and the absorbing capacity of the ILs could be further influenced by substitution of the $[TMGH]^+$ cation. However, most of the gas absorption seems to be due to interactions between the gas molecule and the part of the cation with delocalized π-electrons. Contrary, the anions of the ILs investigated seem to have much less influence on the absorption of the gas. Both Raman and UV–vis spectra indicated week to moderate strength of interaction in the gas-saturated ILs investigated, in good accordance with the estimated standard heats of absorption of -21 to $-37\,kJ\,mol^{-1}$. Ongoing X-ray and Raman spectroscopic investigations [33] on single crystals isolated both from the pure IL, $[TMGH]Tf_2N$, and the IL saturated with SO_2 at 1 bar will hopefully throw more light on the IL solvent–solute interaction and the observed – unusually – high solubility of SO_2 found in these liquids.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.07.036.

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