

# **Ionic Liquids and Acid Gas Capture: Water and Oxygen as Confounding Factors**

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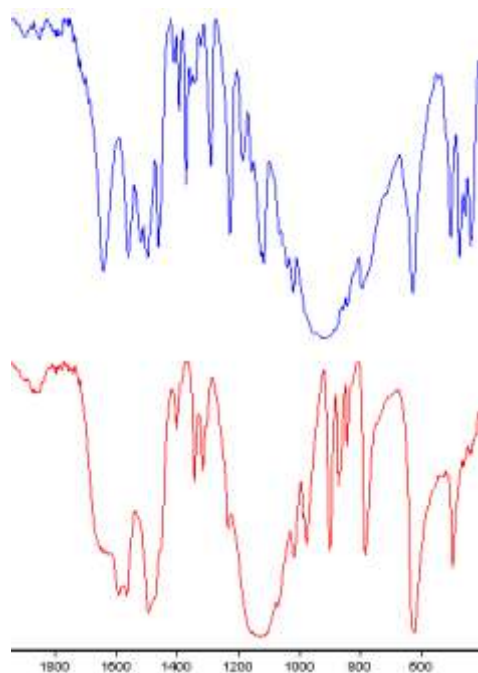
## **SUPPORTING INFORMATION**

## General Experimental

All chemicals were purchased from Sigma-Aldrich Chemical Company and used as delivered except P<sub>66614</sub> Cl (97.7% purity) which was obtained from Cytec Canada Inc. For drying, the IL was dissolved in anhydrous toluene to lower the viscosity and then stirred under vacuum for 6-8 hours at low heat. Gases were purchased from Praxair Canada Inc. and used as delivered, except SO<sub>2</sub> gas (99.9% purity) which was passed through a laboratory gas drying unit filled with CaSO<sub>4</sub>. For anhydrous and anaerobic reactions reagents, including DETA (99%), were dried with stirring under vacuum for several hours prior to use. All inert atmosphere chemistry involving SO<sub>2</sub> was done under argon using double-manifold vacuum lines.

## Instrumental Data

Since all salts formed were found to be soluble only in water, all NMR spectra were obtained in D<sub>2</sub>O. As a result signals due to amino protons do not appear in the spectra. All <sup>1</sup>H NMR spectra were recorded on a Bruker AV 300 spectrometer, <sup>13</sup>C NMR were not obtained due to low solubility of the obtained salts. Infrared spectra were obtained using a Vertex 70 spectrometer, all samples were run as KBr pellets. The "DETA:SO<sub>2</sub>" sample was prepared for infrared analysis in a glove box under argon atmosphere. Elemental analyses were performed with a Perkin Elmer 2400 Series II CHN Analyzer using a cystine standard. The E.A. data obtained for [DETAH<sub>3</sub>][SO<sub>3</sub>][Cl] show large errors which may be attributed to contamination by the ionic liquid in which the crystals were grown. All synthesized salts were observed to be quite hygroscopic, resulting in a small degree of error for each sample.



**Figure S1:**

Infrared spectra of [DETAH<sub>2</sub>][SO<sub>3</sub>]·H<sub>2</sub>O (top) and [DETAH<sub>2</sub>][SO<sub>4</sub>] (bottom) from 2000-400cm<sup>-1</sup>. Note the broad band between 900-1000 cm<sup>-1</sup> (top) which is characteristic of the sulfite salts encountered and the broad band between 1100-1200cm<sup>-1</sup> (bottom) characteristic of the sulfate salts encountered.

## 1. [DETAH<sub>3</sub>][SO<sub>3</sub>][Cl]

### 1.1 Preparation

Crystals were obtained by bubbling SO<sub>2</sub> into a 10% solution of DETA in P<sub>66614</sub> Cl (1mL DETA, 9mL P<sub>66614</sub> Cl) in a flask which was subsequently left under an SO<sub>2</sub> atmosphere for 24-48 hours. The crystals were isolated by vacuum filtration and washed with hexanes in order to lower the viscosity of the ionic liquid which was found to be difficult to filter.

### 1.2 <sup>1</sup>H NMR Data

<sup>1</sup>H NMR (D<sub>2</sub>O, 300 MHz) δ 3.0 (m, 4H), 2.9 (m, 4H)

### 1.3 Infrared Data

3449 (m), 2926 (s), 2120 (w), 1648 (m), 1525 (m), 1465 (m), 1177 (m), 1097 (m), 1021 (s), 973 (s), 867 (s), 626 (m), 506 (m)

## 2. [DETAH<sub>2</sub>][SO<sub>3</sub>]-H<sub>2</sub>O

### 2.1 Preparation

Obtained from a 10% solution of DETA in 95% ethanol (10 mL DETA in 90mL ethanol), SO<sub>2</sub> was bubbled into the solution slowly for approximately 3-5 minutes, yielding a white precipitate that was then isolated through vacuum filtration and washed with ethanol resulting in a white powder which was left to dry under vacuum, yielding 16.3 g (89%). Crystals of [DETAH<sub>2</sub>][SO<sub>3</sub>] were then obtained by dissolving a small amount the powder in water and recrystallizing the product through rotary evaporation of the water.

### 2.2 <sup>1</sup>H NMR Data

<sup>1</sup>H NMR (D<sub>2</sub>O, 300MHz) δ 3.1 (m, 4H), 2.9 (m, 4H)

### 2.3 Infrared Data

3008 (s), 2183 (s), 1636 (s), 1556 (s), 1495 (s), 1360 (m), 1288 (m), 1224 (s), 1116 (s), 1021 (s), 908 (vs, bd), 782 (s), 622 (s), 500(s)

## 2.4 Elemental Analysis

	Theoretical	Actual	% Error
% Carbon	23.64%	23.47%	-0.7%
% Nitrogen	20.67%	19.98%	-3.3%
% Hydrogen	8.64%	8.74%	+1.2%

## 3. [DETAH<sub>2</sub>][SO<sub>4</sub>]

### 3.1 Preparation

Crystals of [DETAH<sub>2</sub>][SO<sub>4</sub>] were obtained from a solution of 10% DETA in P<sub>66614</sub> Cl. The solution had been exposed to SO<sub>2</sub> and left open to air for several weeks (>4) until crystallization.

### 3.2 <sup>1</sup>H NMR Data

<sup>1</sup>H NMR (D<sub>2</sub>O, 300MHz) δ 3.1 (m, 4H), 2.9 (m, 4H)

### 3.3 Infrared Data

3423 (m), 3251 (s), 2075 (w), 1561 (s), 1489 (s), 1388 (w), 1322 (w), 1124 (vs, bd), 1023 (s), 986 (m), 954 (m), 594 (m), 618 (s), 563 (s), 493 (m)

### 3.4 Elemental Analysis

	Theoretical	Actual	% Error
% Carbon	23.87%	24.48%	+2.6%
% Nitrogen	20.88%	20.14%	+3.5%
% Hydrogen	7.51%	8.27%	+10.1%

## 4. "DETA:SO<sub>2</sub>"

### 4.1 Preparation

The complex was obtained by first preparing a 10% solution of DETA in P<sub>66614</sub> Cl (1mL

of DETA in 9mL P<sub>66614</sub> Cl), anhydrous toluene was added to reduce the viscosity of the solution for stirring purposes and the mixture was dried under vacuum for several hours, removing air, water and toluene in the process. The flask was charged with an atmosphere of argon and then evacuated and refilled with SO<sub>2</sub>. The reaction was left to stir for several hours, resulting in the formation of a white precipitate. A KBr pellet of the sample was prepared in a glove box under an argon atmosphere to minimize the duration of air contact during infrared analysis.

## 4.2 Infrared Data

3250 (s), 2930 (s), 2855 (s), 1619 (m), 1543 (m), 1457 (m), 1380 (w), 1196 (m), 1130 (s), 1025 (s), 958 (s), 880 (s), 577 (s)

## 5. Additional Infrared Data

### 5.1 Infrared Data for P<sub>66614</sub> Cl

2956 (s), 2855 (s), 1466 (m), 1112 (w), 988 (w), 813 (w), 721 (w), 429 (s)

### 5.2 Infrared Data for P<sub>66614</sub> Cl with added SO<sub>2</sub>

2956 (s), 2856 (s), 1466 (m), 1271 (m), 1115 (m), 989 (w), 813 (w), 721 (w), 422 (s)

### 5.3 Infrared Data for neat DETA

3354 (m), 3284 (m), 2925 (s), 2860 (s), 1596 (m), 1458 (m), 1352 (w), 1303 (w), 1126 (m), 1070 (m), 891 (m), 836 (m)

## 6. Crystallographic Data

### 6.1 General

In all studies the crystals were attached to the tip of a nylon loop with paratone-N oil. All measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 mV) using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 100 K, except for [DETAH<sub>2</sub>][SO<sub>3</sub>] $\cdot$ H<sub>2</sub>O where the data was collected at room temperature. The initial orientation and unit cell were indexed using a least-squares analysis of a random set of

reflections collected from three series of  $0.5^\circ$   $\omega$ -scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four  $\omega$ -scan frame series were collected with  $0.5^\circ$  wide scans, 30 second frames and 606 frames per series at varying  $\varphi$  angles ( $\varphi = 0^\circ, 90^\circ, 180^\circ, 270^\circ$ ). The crystal to detector distance was set to  $\sim 6$  cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS). The structures were solved using direct methods (SHELXS-97) and refined by full-matrix least-squares method on  $F^2$  with SHELXL-97. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealized positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at  $1.2U_{\text{eq}}$  of the parent carbon atom,  $1.5U_{\text{eq}}$  for methyl hydrogens. Hydrogen atoms bonded to oxygen and/or nitrogen were treated in one of two ways. The positions of hydrogen atoms of water molecules were located in near final Fourier difference maps and selected based on hydrogen bonding considerations. They were placed in those positions and allowed to refine isotropically with a weak distance restraint imposed. The H(N) hydrogen atoms were allowed to refine isotropically, with a weak restraint placed on the N-H bond length to keep it reasonable if required. Important details of the individual refinements are given below.

## 6.2 [DETAH<sub>3</sub>] [SO<sub>3</sub>] [Cl]

This structure of [DETAH<sub>3</sub>] [SO<sub>3</sub>] [Cl] was first solved in the monoclinic space group  $P2_1/c$ , with a unit cell of  $a = 10.764(5)$ ,  $b = 9.727(4)$ ,  $c = 9.874(4)$  Å and  $\beta = 111.877(4)^\circ$ . In this space group the entire cation and all atoms of the anions are unique and present with full occupancy. The final R factor was determined to be 0.0362 for 1842 reflections with  $I > 2\sigma(I)$ . However, the Checkcif report indicated that an additional symmetry element had been detected. Redetermination of the unit cell located a smaller monoclinic cell, with  $a = 4.936(3)$ ,  $b = 9.726(5)$ ,  $c = 10.030(5)$  Å and  $\beta = 95.299(5)^\circ$ . The new space group  $P2_1/m$  generates a mirror plane on which sit N1, H1 and H2 of the cation and S1 and Cl1 of the anions. As a result only one half of the cation is unique, with the other half generated by reflection. This also results in the SO<sub>3</sub><sup>2-</sup> anion being disordered, with pairs of oxygen atoms being generated by reflection across the mirror plane. To keep O1 off the mirror plane, the distance between O1 and its symmetry equivalent O1A was restrained to 0.40(0.015) Å. Refinement in this space group gave  $R1 = 0.0324$  for 1101 reflections with  $I > 2\sigma(I)$  with 50 fewer refined parameters. The results of the second refinement are presented in this work.

### 6.3 [DETAH<sub>2</sub>][SO<sub>3</sub>] $\cdot$ H<sub>2</sub>O

The refinement of the structure of [DETAH<sub>2</sub>][SO<sub>3</sub>] $\cdot$ H<sub>2</sub>O was uneventful until location of the hydrogen atoms was attempted. At this point the heavy atoms (cation, anion and oxygen of a presumed hydrating water molecule) had been refined anisotropically and the H(C) atoms had been placed geometrically in the structure. The position of these atoms was certain but the location of the remaining hydrogen atoms was more ambiguous. After much work, the asymmetric unit was shown to contain H<sub>2</sub>O, DETAH<sub>2</sub><sup>2+</sup> and SO<sub>3</sub><sup>2-</sup>. To balance the charge, the proton on the central nitrogen (N1) is disordered over two positions each with an occupancy of one half, while both terminal nitrogens are fully protonated. The water molecule is also disordered (having one hydrogen with full occupancy and the other disordered over two half occupancy positions). This gives rise to two distinct hydrogen bonding motifs running through the structure, their nature being determined by which proton sites are filled on the central nitrogen of the cation and on oxygen of the water molecule. A full description of the solution, including rationale for the hydrogen atom placement and a detailed diagram and explanation of the hydrogen bonding, will be published subsequently.

Table S1. Crystal data and structure refinement details for the reported complexes.

Identification code	[DETAH <sub>3</sub> ][SO <sub>3</sub> ][Cl]	[DETAH <sub>2</sub> ][SO <sub>3</sub> ].H <sub>2</sub> O
Empirical formula	C <sub>4</sub> H <sub>16</sub> ClN <sub>3</sub> O <sub>3</sub> S	C <sub>4</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> S
Formula weight	221.71	203.27
Temperature (K)	100(2)	299(2)
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>P</i> -1
Unit cell dimensions (Å, °)	<i>a</i> = 4.936(3) <i>b</i> = 9.726(5) <i>c</i> = 10.030(5) <i>α</i> = 90 <i>β</i> = 95.299(5) <i>γ</i> = 90	6.746(3) 8.502(4) 9.273(4) 110.552(4) 95.519(5) 94.516(5)
Volume (Å <sup>3</sup> )	479.5(4)	492.0(4)
<i>Z</i>	2	2
Density (calc., Mg/m <sup>3</sup> )	1.535	1.372
Absorption coeff. (mm <sup>-1</sup> )	0.593	0.316
F(000)	236	220
Crystal size (mm <sup>3</sup> )	0.14, 0.12, 0.08	0.20, 0.18, 0.02
Theta range of data	2.04 / 28.84	2.37 / 28.86
Reflections collected	5790	5954
Independent refl., R(int)	1260 / 0.0269	2358 / 0.0300
Completeness (%), theta (°)	99.8 / 25.00	99.6 / 26.00
Max./min. transmission	0.9541 / 0.9216	0.9937 / 0.9395
Data/ rest./parameters	1260 / 6 / 91	2358 / 11 / 153
Goodness-of-fit on F <sup>2</sup>	1.063	1.044
R indices(2σ(I)),R1/wR2	0.0324 / 0.0802	0.0344 / 0.0881
R indices(all data),R1/wR2	0.0386 / 0.0841	0.0422 / 0.0934
Largest diff. peak/hole(e.Å <sup>-3</sup> )	0.732 / -0.256	0.226 / -0.277



Table S2. Hydrogen bonds in the reported compounds.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
<b>[DETAH<sub>3</sub>][SO<sub>3</sub>][Cl]</b>				
N(1)-H(1)...O(3)	0.98(4)	1.85(3)	2.798(3)	160(2)
N(1)-H(1)...O(3)#1	0.98(4)	1.85(3)	2.798(3)	160(2)
N(1)-H(2)...O(3)#2	0.89(1)	1.89(1)	2.751(3)	163(2)
N(1)-H(2)...O(3)#3	0.89(1)	1.89(1)	2.751(3)	163(2)
N(2)-H(3)...Cl(1)#4	0.90(1)	2.32(2)	3.172(2)	158(2)
N(2)-H(4)...O(2)#1	0.90(1)	1.90(2)	2.738(3)	154(2)
N(2)-H(4)...O(3)	0.90(1)	2.11(2)	2.942(3)	153(2)
N(2)-H(5)...O(1)#5	0.88(1)	1.91(2)	2.770(2)	165(3)
N(2)-H(5)...O(1)#6	0.88(1)	2.06(2)	2.917(4)	164(2)
C(1)-H(1A)...Cl(1)	0.99	2.79	3.718(2)	156.7
C(1)-H(1B)...Cl(1)#7	0.99	2.86	3.668(2)	139.5
C(2)-H(2A)...Cl(1)#8	0.99	2.84	3.726(2)	149.8
C(2)-H(2B)...O(2)#6	0.99	2.44	3.211(3)	134.7
C(2)-H(2B)...O(3)#2	0.99	2.43	3.231(3)	137.9
C(2)-H(2B)...O(2)#3	0.99	2.55	3.530(3)	171.1
<b>[DETAH<sub>2</sub>][SO<sub>3</sub>]·H<sub>2</sub>O</b>				
N(1)-H(1)...O(4)	0.88(2)	2.48(2)	3.319(3)	161(3)
N(1)-H(2)...O(4)#9	0.85(2)	2.19(2)	3.009(2)	162(3)
N(2)-H(3)...O(1)#10	0.90(2)	1.95(2)	2.821(2)	162(2)
N(2)-H(4)...O(4)	0.90(2)	2.00(2)	2.896(2)	176(2)
N(2)-H(5)...O(3)#11	0.87(2)	1.93(2)	2.768(2)	163(2)
N(3)-H(6)...O(3)#12	0.89(2)	1.96(2)	2.857(2)	174(2)
N(3)-H(7)...O(2)#13	0.87(2)	1.90(2)	2.776(2)	179(2)
N(3)-H(8)...O(1)	0.90(2)	1.90(2)	2.801(2)	178(2)
O(4)-H(9)...O(2)	0.80(2)	1.89(2)	2.689(2)	174(3)
O(4)-H(10)...O(4)#14	0.80(2)	2.12(3)	2.853(4)	152(5)
O(4)-H(11)...N(1)	0.82(2)	2.67(5)	3.319(3)	137(6)
O(4)-H(11)...N(1)#9	0.82(2)	2.39(5)	3.009(2)	133(6)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z #2 x-1,y,z #3 x-1,-y+3/2,z #4 -x+1,-y+1,-z+1 #5 -x+1,-y+1,-z  
 #6 -x+1,y-1/2,-z #7 x+1,y,z #8 -x,-y+1,-z+1 #9 -x,-y+2,-z #10 x,y+1,z  
 #11 -x+1,-y+2,-z+1 #12 x-1,y,z #13 -x,-y+1,-z #14 -x+1,-y+2,-z

Table S3. Sulfite anion geometries, bond lengths [Å] and angles [°].

	[DETAH <sub>3</sub> ][SO <sub>3</sub> ][Cl]	[DETAH <sub>2</sub> ][SO <sub>3</sub> ·H <sub>2</sub> O]	[NH <sub>4</sub> ] <sub>2</sub> [SO <sub>3</sub> ·H <sub>2</sub> O]
S(1)-O(1)	1.533(2)	1.5224(12)	1.532
S(1)-O(2)	1.539(2)	1.5224(13)	1.520
S(1)-O(3)	1.550(2)	1.5211(13)	1.535
O(1)-S(1)-O(2)	103.96(9)	104.80(6)	105.4
O(1)-S(1)-O(3)	102.03(13)	104.31(7)	104.4
O(2)-S(1)-O(3)	103.55(12)	104.76(7)	104.6

[NH<sub>4</sub>]<sub>2</sub>[SO<sub>3</sub>·H<sub>2</sub>O data is taken from Battelle and Trueblood, *Acta Cryst.* (1965) **19**, 531-535. The bond lengths quoted are after correction for libration. The esd's of the S-O distances are about 0.006 Å and of the O-S-O angles about 0.4°.

## References

- [1] APEX2 (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.
- [2] SAINT (Bruker, 2008) Bruker AXS Inc., Madison, Wisconsin, USA.
- [3] SADABS (Bruker, 2009) Bruker AXS Inc., Madison, Wisconsin, USA.
- [4] Sheldrick, G.M. (2008). *Acta Cryst.*, A64, 112-122.