

# A reversible zwitterionic SO<sub>2</sub>-binding organic liquid†

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*N,N*-Dibutylundecanolamine is a liquid that chemically binds SO<sub>2</sub> to form a viscous zwitterionic liquid that contains 35% by wt. SO<sub>2</sub> at standard temperature and pressure. SO<sub>2</sub> is chemically bound to the alcohol component as an alkylsulfite, which is then stabilized by the amine. The zwitterionic liquid can be reverted to its non-ionic form and recycled by thermally stripping the SO<sub>2</sub> under vacuum at temperatures near 70 °C. *N,N*-Dibutylundecanolamine is a potential flue gas desulfurizing solvent because it is chemically selective to bind SO<sub>2</sub> but not basic enough to chemically bind CO<sub>2</sub>.

## Introduction

As fossil fuel consumption continues, there is much attention being focused on capturing acid gas emissions from power plants. We have recently investigated SO<sub>2</sub>-binding organic liquids (SO<sub>2</sub>BOLs) as means to reversibly capture and release SO<sub>2</sub> selectively over CO<sub>2</sub>.<sup>1</sup> SO<sub>2</sub>BOLs are mixtures of tertiary amines and alcohols, which bind SO<sub>2</sub> as liquid ammonium alkylsulfite salts. Tertiary amines selectively bind SO<sub>2</sub> over CO<sub>2</sub> because tertiary amines are basic enough to accept a proton from sulfurous and alkylsulfurous acids but not carbonic or alkylcarbonic acids. Other groups have absorbed SO<sub>2</sub> physically in ionic liquids<sup>2–4</sup> or chemically absorb SO<sub>2</sub> in organic systems<sup>5–7</sup> or as irreversible aqueous bisulfite or sulfite salts.<sup>8–11</sup>

We believed that a bifunctional tertiary alkanolamine would be able to capture SO<sub>2</sub> comparable to our binary SO<sub>2</sub>BOL system. We

present here a reversible zwitterionic liquid produced from the reaction of SO<sub>2</sub> with *N,N*-dibutylundecanolamine (DBUA). The SO<sub>2</sub> is chemically bound through the alcohol moiety as an alkylsulfite, which we believe is stabilized by hydrogen bonding through the protonated amine portion of the molecule.

Our recent interest in SO<sub>2</sub>BOLs led us to explore the possible reaction of tertiary alkanolamines with SO<sub>2</sub> to form reversible zwitterionic liquids. Pairing the base and the alcohol on one molecule provides reduced volatility of the base and alcohol components and provides unimolecular phase behaviour compared to bimolecular reversible ionic liquid systems. To our knowledge there are few examples of zwitterionic liquids, and none of them have been shown to be reversible (polar to non-polar).<sup>12–14</sup> Our first target molecule was DBUA because we envisioned long alkyl chains keeping the alkanolamine as a liquid before and after exposure to SO<sub>2</sub>. *N,N*-Dibutylundecanolamine was synthesized in 88% isolated yield by refluxing dibutylamine and 11-bromoundecanol in ethanol (Fig. 1).

The isolated DBUA was a clear and yellow viscous liquid. Spectroscopic characterization of DBUA was performed using both <sup>1</sup>H in CDCl<sub>3</sub> and <sup>13</sup>C NMR of the neat liquid (Table 1). The <sup>1</sup>H NMR of the free DBUA in CDCl<sub>3</sub> showed the R-CH<sub>2</sub>-O hydrogens (1 using the numbering scheme in Fig. 2) as a triplet at 3.65 ppm. All three R-CH<sub>2</sub>-N hydrogens (11,12) were observed as a triplet at 2.4 ppm. Terminal CH<sub>3</sub> triplets on the butyl chains (15) were seen at 0.9 ppm. The remaining internal CH<sub>2</sub> hydrogens in the butyl and undecyl chains (2–10,13,14) were observed as complex multiplets from 1.2 to 1.6 ppm. The O–H was not observed likely because of overlap of other hydrogen peaks. The infrared (IR) spectrum of DBUA neat on NaCl disks showed a strong and broad O–H band at 3333 cm<sup>-1</sup>, and aliphatic C–H bands at 2800–3000 cm<sup>-1</sup>.

Anhydrous DBUA when exposed to one equivalent of SO<sub>2</sub> generates a highly viscous yellow liquid, which we assign to be the zwitterion (Fig. 3). Amine and alcohol blends have been shown to increase in viscosity when a liquid alkylsulfite salt is produced.<sup>1</sup> After one equivalent of SO<sub>2</sub> is chemically absorbed to form the zwitterion,

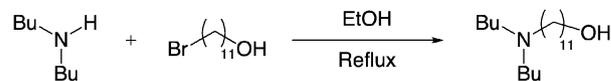


Fig. 1 Synthetic route for making DBUA.

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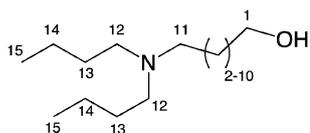
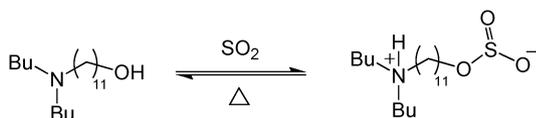
## Broader context

With global consumption of energy derived from carbon-based fuels expected to continue rising, capturing greenhouse gases other than CO<sub>2</sub> becomes a necessity. SO<sub>2</sub> is a major component of acid rain, and is captured using aqueous lime and caustic soda solutions, which are corrosive, and irreversible. While SO<sub>2</sub> is considered a waste product, it can be recovered and used in the wine and cement industries rather than being permanently sequestered. It was our goal to design a more environmentally benign solvent system that can reversibly capture SO<sub>2</sub> as well as use it as a solvent miscibility trigger.

**Table 1** NMR chemical shifts of DBUA in CDCl<sub>3</sub> with and without SO<sub>2</sub>

<sup>1</sup> H <sup>a</sup>	1	11,12	2–10,13,14	15	O–H N–H
DBUA	3.65	2.40	1.3–1.6	0.9	—
DBUA-SO <sub>2</sub>	3.70	2.95	1.3–1.7	0.9	10.2
<sup>13</sup> C <sup>b</sup>	1	11,12	13–15	2–10	—
DBUA	61.6	54.3, 53.9	33.1–20.8	14.2	—
DBUA-SO <sub>2</sub>	61.0	52.5	31.4–20.6	14.2	—

<sup>a</sup> CDCl<sub>3</sub> referenced to TMS. <sup>b</sup> neat.

**Fig. 2** Numerical assignment of DBUA.**Fig. 3** Reaction of DBUA with SO<sub>2</sub>.

the viscosity then begins to decrease as more SO<sub>2</sub> is physically absorbed in the ionic liquid. Physically absorbed SO<sub>2</sub> in an ionic liquid acts like a molecular lubricant which has been shown to reduce the viscosity of numerous ionic liquids.<sup>2–4</sup> The zwitterion was soluble in CDCl<sub>3</sub> and MeCN and was fully characterized by NMR. The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showed minimal downfield shifting of the R-CH<sub>2</sub>-O protons (1) from 3.65 to 3.70. Slight shifting of the protons (1) was also observed in our previous studies of alkylsulfites, which we attributed to the shielding of the CH<sub>2</sub> protons by the large sulfur atom counteracting the electronegativity of the sulfoxylate anion.<sup>1</sup> The three R-CH<sub>2</sub>-N protons (11,12) on the amine functionality were all observed at 2.95 ppm, 0.5 ppm downfield from the unbound DBUA at 2.40 ppm. The 0.5 ppm downfield shifting is in agreement with other ammonium alkylsulfite salts.<sup>1</sup> The spectrum showed a broad singlet centered at 10.2 ppm corresponding to the protonated amine [N–H]<sup>+</sup>. The viscous liquid is not likely a sulfonamide-like salt because the amine is sterically hindered. The <sup>13</sup>C spectrum of the neat zwitterion showed minor upfield shifting of the R-CH<sub>2</sub>-O (1) carbon by 0.6 ppm and the R-CH<sub>2</sub>-N (11,12) carbons by 1.6 ppm. The <sup>1</sup>H and <sup>13</sup>C chemical shifts are in agreement with other liquid alkylsulfite salts.<sup>1</sup> High resolution mass spec (+mode analysis) of the DBUA matched the expected DBUA +1 peak, however the zwitterion molecular ion peak was not depleted because SO<sub>2</sub> had been cleaved under ionizing conditions and only the DBUA +1 peak was observed.

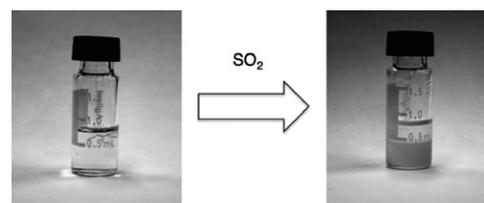
The infrared (IR) spectrum of the neat zwitterion on NaCl plates showed the strong O–H band had been replaced by a weak N–H band at 3384 cm<sup>-1</sup>. Medium intensity [R<sub>3</sub>N–H]<sup>+</sup> bands were observed at 2646 and 2548 cm<sup>-1</sup> similar to trialkylammonium salts.<sup>15</sup> Strong ROSO<sub>2</sub><sup>-</sup> bands appeared at 1322, 1170, and 678 cm<sup>-1</sup>, which are in agreement with other sulfite salts.<sup>1,16,17</sup> After SO<sub>2</sub> stripping, the ROSO<sub>2</sub><sup>-</sup>, N–H and [R<sub>3</sub>N–H]<sup>+</sup> bands disappeared, and the O–H band reappeared. Crystallographic analysis could not be performed because the zwitterion was a liquid.

DBUA was unreactive towards CO<sub>2</sub>. An NMR sample (10 mg DBUA in 0.8 mL of CDCl<sub>3</sub>) was sparged for ten minutes with CO<sub>2</sub> and then characterized by <sup>1</sup>H NMR. There was no mass increase in the sample associated with CO<sub>2</sub> uptake, nor was there a change in the <sup>1</sup>H NMR spectrum of DBUA in the presence of CO<sub>2</sub>. The same NMR sample was then sparged with SO<sub>2</sub> for 5 minutes and spectroscopically characterized. The <sup>1</sup>H NMR spectrum matched that of DBUA-SO<sub>2</sub>, indicating SO<sub>2</sub> was bound by DBUA. The ability of DBUA to capture SO<sub>2</sub> and not CO<sub>2</sub> suggests chemically selective desulfurization of gas streams is possible.

One milliliter of DBUA (0.96 grams, 3.3 mmol) absorbed 0.52 grams (8.1 mmol) of SO<sub>2</sub>, 35% SO<sub>2</sub> by weight (0.21 g chemical, 0.31 g physical). The zwitterion did not liberate gas at room temperature, however it did liberate gas as temperature was increased. The physically absorbed SO<sub>2</sub> can be removed by heating the zwitterion or by placing it under vacuum at room temperature. The chemically bound SO<sub>2</sub> is more difficult to strip. It can be removed at 70 °C with a nitrogen sparge overnight, or a more rapid stripping of SO<sub>2</sub> can be done in 40 minutes at 70 °C under vacuum. The DBUA can be quantitatively recovered (3.3 mmol, >99%) after SO<sub>2</sub> stripping. The DBUA was exposed to SO<sub>2</sub> and subsequently stripped for 2 cycles; both cycles showed absorption of 8.1 mmol of SO<sub>2</sub> and complete stripping of SO<sub>2</sub> without any significant loss of material. DBUA is predicted to be recycled indefinitely as long as there is no contact with moisture, wherein a thermally stable bisulfite salt would be produced.

The polarity switching of DBUA between its nonionic and zwitterionic forms was demonstrated by placing 0.35 mL of DBUA and 0.35 mL of hexanes (Fig. 4) in a glass vial. DBUA was miscible with hexanes until SO<sub>2</sub> was sparged through the solution until one molar equivalent of SO<sub>2</sub> had been chemically bound (10 minutes at 0 °C). The hexanes partitioned out into a separate phase when DBUA was converted into its more polar zwitterionic form.

SO<sub>2</sub> is chemically bound on the alcohol component of DBUA as an alkylsulfite and not a sulfonamide because of the steric hindrance of the amine functionality. The alkyl chains on the nitrogen prohibit access of the amine to coordinate to SO<sub>2</sub>, leaving the alcohol as the lone nucleophilic center on the molecule. SO<sub>2</sub> reacts with alcohols to form thermodynamically unstable alkylsulfonic acids comparable to

**Fig. 4** Left: DBUA and hexanes, Right: DBUA-SO<sub>2</sub> and hexanes.

SO<sub>2</sub> reacting with water to form sulfurous acid. Alkylsulfonic acids are likely to be stabilized in the presence of non-nucleophilic organic bases to form alkylsulfite salts similarly to alkylcarbonic acids which can be stabilized by strong organic bases.<sup>1,18–22</sup> We predict that the zwitterion is a liquid because of the large undecanyl group between the cationic and anionic portions of the molecule as well as the butyl groups on the nitrogen. We are currently investigating the binding energies and kinetics of SO<sub>2</sub> absorption in comparison to our dual component SO<sub>2</sub>BOL systems. Investigations of the effect of alkyl chain length of the amines and the alkyl spacer between the amines and alcohol to determine the effect of spacing on the physical properties of the resulting zwitterions.

In conclusion, DBUA reversibly reacts with SO<sub>2</sub> to form a room temperature, reversible zwitterionic liquid. The SO<sub>2</sub> is chemically bound through the alcohol as an alkylsulfite, which is stabilized by the base component. The zwitterion can contain up to 35% by weight SO<sub>2</sub>, and can be thermally reversed at 70 °C. The reversible zwitterion can be applied to phase separation chemistry and selective desulfurization of gas streams.

## Experimental section

All reactions were run under an atmosphere of argon, unless otherwise indicated. Solvents were transferred by a plastic syringe. Flasks were oven-dried and cooled under a stream of argon. Ethanol was purchased from Fisher and used without further purification. SO<sub>2</sub> was purchased from the Aldrich chemical company and used without purification. High-resolution mass spectra (HRMS) were obtained on a LTQ Orbitrap™ Mass Spectrometer from Thermo Scientific Company as m/e (relative intensity). Accurate masses are reported for the molecular ion (M + 1) or a suitable fragment ion. IR measurements were performed on NaCl disks using a Nicolet Magna-750 spectrometer running on OMNIC software. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded with a Varian (300 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were recorded with a Varian 300 (75.5MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the singlet of the terminal CH<sub>3</sub> on the butyl groups of dibutylamine at 14.2 ppm.

11-(*N,N*-Di-*n*-butylamino)-1-undecanol (DBUA) was prepared according to a modified literature procedure.<sup>23</sup> Dibutylamine (9.4 mL, 55.70 mmol) and 11-bromo-1-undecanol (4.0g, 15.92 mmol) were charged into a clean dry 250 mL flask. Ethanol (100 mL) was added, the resulting solution was heated to reflux under an argon atmosphere for 18 h at which point the reaction mixture was allowed to cool to room temperature and then the solvent was removed in *vacuo* to afford a white solid. This crude product was dissolved in water (100 mL), and the pH was adjusted to 9.0 using solid Na<sub>2</sub>CO<sub>3</sub>. This solution was extracted with CHCl<sub>3</sub> (3 × 30 mL), the organic layers were combined, dried over MgSO<sub>4</sub>, filtered, and then concentrated to provide a pale yellow oil. Excess dibutylamine was distilled off under vacuum at 90 °C. The final product was recovered as a pale yellow oil (4.2g, 88% yield.)

DBUA was syringed into oven-dried round bottom flask fitted with a rubber septa and weighed. The septa was punctured with

a needle connected to a N<sub>2</sub> bubbler and a polyetheretherketone (PEEK) 1/16" tube connected to a lecture bottle of SO<sub>2</sub>. The flask was placed in an ice water bath and then DBUA was sparged with SO<sub>2</sub> to form the zwitterion. The formation of DBUA-SO<sub>2</sub> was very exothermic and was kept cold until only physically absorbed SO<sub>2</sub> was dissolving into the zwitterionic liquid. The sample was continually sparged with SO<sub>2</sub> while the flask was warmed to 25 °C. Once the uptake had finished, the flask was quickly vacuumed and refilled with N<sub>2</sub> three times to remove any gaseous SO<sub>2</sub> in the flask. The flask was then weighed to record the SO<sub>2</sub> gravimetric uptake at 25 °C.

Stripping of SO<sub>2</sub> was performed by placing DBUA-SO<sub>2</sub> and a 1" stir bar in a flask fitted with a jacketed condenser. The flask was then placed in an oil bath set to 70 °C under vacuum. The flask was heated under vacuum for 40 minutes while stirring. The flask was then cooled and weighed.

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