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# Kinetics and pathways for nitrosamine formation in amino acid-based carbon dioxide capture systems

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## ABSTRACT

Amino acids are emerging as alternative solvents for absorption-based $CO_2$ capture, but their potential to form the harmful byproducts nitrosamines is not well understood. This study investigated the formation of nitrosamines from model amino acids sarcosine, proline, and taurine under desorber- and absorber-relevant conditions. Special attention was paid to the effects of base and the formation of volatile nitrosamines. Under simulated desorber conditions, all three amino acid solvents with organic base monoethanolamine (MEA) formed more total nitrosamines than those with inorganic base sodium hydroxide (NaOH). Increasing base concentration decreased the formation of *N*-nitrososarcosine (NSAR) in both NaOH- and MEA-based sarcosine solvents. By measuring NSAR formation under varying base concentration and $CO_2$ loading, it was shown that both sarcosine carbamic acid (SARCOOH) and deprotonated sarcosine ($SAR^-$) contributed to NSAR formation. Volatile nitrosamine *N*-nitrosodimethylamine (NDMA) was detected in sarcosine solvents at levels three orders of magnitude lower than NSAR. Kinetic modeling showed that 61%–110% of the accumulated NDMA was formed through NSAR decomposition. NDMA formation from NSAR was promoted by increasing MEA concentration, but suppressed by increasing NaOH concentration. Under simulated absorber conditions, NaOH- and MEA-based solvents formed total nitrosamines at similar rates for sarcosine, proline, and taurine. In sarcosine solvents, NDMA formed at levels three orders of magnitude lower than NSAR, similar to that under desorber conditions.

## 1. Introduction

Climate change is one of the most challenging environmental problems of our times. More than three quarters of the total amount of greenhouse gases emitted in 2010 was carbon dioxide ($CO_2$) (Edenhofer et al., 2014). Anthropogenic $CO_2$ emissions have increased by 86% from 1980 to 2014 (Boden et al., 2017). Globally, fossil fuel-fired power plants are the largest anthropogenic sources of $CO_2$ (International Energy Agency, 2016). According to the U.S. Energy Information Administration (2017), fossil fuels will likely continue to dominate global power market in the next few decades. Carbon capture and storage is an important strategy to timely control $CO_2$ emissions in order to mitigate climate change (Metz et al., 2005). Post-combustion $CO_2$ capture systems can be retrofitted into existing power plants, reducing up to 90% of $CO_2$ emissions (Rao and Rubin, 2002). Beneficial use of the captured $CO_2$ for enhanced oil recovery has been implemented to offset the cost of $CO_2$ capture (van Bergen et al., 2004).

Amine-based absorption is the most mature technology for post--combustion $CO_2$ capture (Bhown and Freeman, 2011). In a typical absorption system, flue gas is introduced to the absorber (40–60 °C) to counter-currently contact with the solvent (e.g., 2.5–8 M or 15–50 wt% amine solutions), through which 75–90% of $CO_2$ is removed (Rao and Rubin, 2002). Treated flue gas is emitted to the atmosphere directly or after being scrubbed by a washwater unit. The $CO_2$-rich solvent is pumped to the desorber for regeneration under high temperatures (e.g., 100–140 °C) (Kuckshinrichs and Hake, 2014), and then circulated back to the absorber through a heat exchanger. The released $CO_2$ is compressed for storage or beneficial use. Most commercial solvents are aqueous amine solutions. Monoethanolamine is (MEA) is the benchmark solvent and has been used in an industrial scale $CO_2$ capture facility in Saskatchewan, Canada (Gouedard et al., 2012; Zhao et al., 2013).

Despite the maturity of the amine-based $CO_2$ capture technology, challenges remain regarding its operational cost and environmental impacts. Because the relatively high volatility of amines contributes to both of these challenges (Karl et al., 2011; Nguyen et al., 2010; Zhang et al., 2012), amino acid salts and other ionic liquids are emerging as a group of alternative solvent chemicals (Kumar et al., 2003; Orhan et al.,

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2016; Orhan and Alper, 2017). In the presence of base (i.e., at high pH), the amino group in amino acids exhibits similar affinity towards $CO_2$ as that in their amine analogues (Thee et al., 2014); meanwhile, the carboxyl group, present in the anionic form, substantially reduces the volatility of the molecules (van Holst et al., 2009). Both inorganic (e.g., sodium or potassium hydroxide) and organic bases (e.g., MEA) have been used in amino acid solvents to maintain deprotonation of the amino and carboxyl functional groups (Ciftja et al., 2013). Amino acid solvents potassium prolinate and potassium glycinate showed 2.8 and 1.6 times higher $CO_2$ absorption rate than MEA, respectively (van Holst et al., 2009).

The major environmental impacts of the amine technology are associated with the formation and emission of nitrosamine byproducts. Nitrosamines are formed when $NO_x$ in the flue gas reacts with amines in the solvent. Additionally, nitrite, a $NO_x$ hydrolysis product, reacts with amines in the desorber to form more nitrosamines. Bench-scale studies showed that more nitrosamines were formed by secondary and tertiary amines, such as morpholine, piperazine, triethanolamine, and *N*-methyldiethanolamine, than by primary amine MEA (Chandan et al., 2013; Dai and Mitch, 2013, 2014; Fine et al., 2014a; Yu et al., 2016). A regulatory example for nitrosamines is the discharge permit issued by the Norwegian Climate and Pollution Agency for the proposed $CO_2$ Technology Centre Mongstad facility, which limited the sum of all nitrosamines and nitramines to 0.3 ng/m$^3$ in downwind airsheds and 4 ng/L in downwind water supplies (Norwegian Climate and Pollution Agency, 2011).

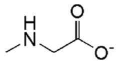
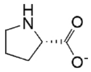
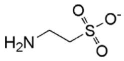
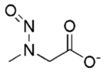
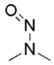
To date, information has been scarce regarding nitrosamine formation in amino acid solvents. Due to the structural similarity between amino acids and amines, amino acids are expected to also undergo nitrosation on the amino group, but the reactions can be influenced by the carboxyl group or the presence of base in the solvents. This study investigated the kinetics and reaction pathways for nitrosamine formation in amino acid solvents under simulated desorber and absorber conditions. First, three amino acids, sarcosine, L-proline, and taurine that were previously shown to feature relatively high $CO_2$ capture rates (Aronu et al., 2010; Ciftja et al., 2013; Thee et al., 2014; van Holst et al., 2009) were evaluated. Special attention was paid to the effects of base, because it is a crucial component of amino acid solvents. Second, using sarcosine as a model amino acid, the kinetics and mechanisms for nitrosamine formation were investigated. Third, a kinetic model was developed for the formation of the volatile nitrosamine *N*-nitrosodimethylamine (NDMA) in sarcosine solvents. NDMA was selected as a target volatile nitrosamine due to a previous report of its presence in the washwater of a laboratory-scale sarcosine system (Dai and Mitch, 2013). Lastly, nitrosamine formation in the three amino acid solvents was evaluated under simulated absorber conditions.

## 2. Materials and methods

### 2.1. Materials

The following chemicals were obtained from Sigma–Aldrich: sarcosine (≥98%), L-proline (≥99%), taurine (≥99%), sodium bicarbonate (≥99.7%), sodium nitrite (≥99%), sulfamic acid (99.3%–100.3%), ethanolamine (MEA, ≥99%), *N*-nitrosodimethylamine-$d_6$ (≥98%) and *N*-nitrosodimethylamine (≥99.9%). The following chemicals were obtained from Fisher Scientific: sodium hydroxide (NaOH) (99.1%), acetonitrile (HPLC grade, 99.9%), methanol (HPLC grade, 99.9%), potassium phosphate, monobasic (99.6%), and methylene chloride (HPLC grade, 99.9%). The color reagent for nitrite determination (sulfanilamide/N-(1-naphthyl) ethylenediamine dihydrochloride solution) was purchased from Ricca Chemical. Potassium iodide (≥99%), iodine resublimed, tetrabutylphosphonium hydroxide ($P_{4444}OH$) (40 wt% in water), and tetrabutylammonium hydroxide ($N_{4444}OH$) (40 wt% in water) were purchased from Acros. Sulfuric acid (95–98%) and glacial acetic acid (99.9%) were purchased from J.T. Baker. Anhydrous sodium sulfate was purchased from Macron Fine Chemicals. Hydrochloric acid (normality: 5.950–6.050 N) was purchased from BDH Chemicals. Phosphoric acid (85%) was purchased from Mallinckrodt. Nitrogen gas (industrial grade), oxygen gas (industrial grade), carbon dioxide gas (industrial grade), 1000 ppm nitric oxide balance nitrogen, and 1000 ppm nitrogen dioxide balance nitrogen were purchase from Jackson Welding and Gas Products. All chemicals were used as received without further purification. The structure of amino acids and nitrosamines investigated in this study are listed in Table 1.

**Table 1**
Amino acids and nitrosamines investigated in this study.

| Name | Abbreviation | Structure |
|---|---|---|
| *Amino acids (anionic form)* | | |
| Sarcosinate | – |  |
| Prolinate | – |  |
| Taurinate | – |  |
| *Nitrosamines* | | |
| *N*-Nitrososarcosine | NSAR |  |
| *N*-Nitrosodimethylamine | NDMA |  |

### 2.2. Sample preparation

The amino acid solvents for desorber experiments were prepared as mixtures of amino acid, base, sodium bicarbonate, and sodium nitrite. Amino acids were added gravimetrically to achieve the target concentration. Two bases, NaOH and MEA, were evaluated in the experiments. A concentrated NaOH stock solution (8 M) was prepared freshly before use. MEA was added to the amino acid solutions gravimetrically. Sodium bicarbonate was added to obtain the target C/N molar ratios (0–0.2). A sodium nitrite stock solution (200 mM) was added last to the solvents to obtain the designated initial nitrite concentrations. Each 10 mL of freshly prepared amino acid solvents was transferred to a Swagelok stainless steel tube (6 inch in length, 0.4 inch in inner diameter). The tubes were placed in a convection oven set at the reaction temperature (120 °C). The tubes were removed from the oven at set time points and cooled immediately in a water bath.

For the simulated absorber experiments, amino acid solvents were prepared similarly, except that sodium bicarbonate and sodium nitrite were not added. The amino acid solvent (50 mL) was placed in a 125 mL Pyrex® gas washing cylinder bottle with fritted disc. The bottle was placed in a water bath maintained at 30 °C. The solvent was continuously purged with a stream of synthetic flue gas at a flow rate of 413 mL/min. The composition of the gas was 10 ppm $NO_2$, 100 ppm NO, 3.2% $CO_2$, 13.6% $O_2$, and 72.6% $N_2$.

### 2.3. Sample analysis

Nitrite was measured using the standard *N*-(1-naphthyl)ethylenediamine dihydrochloride colorimetric method (Clesceri et al., 1998). Solvent samples were diluted 100–1000 times with Milli-Q water to obtain nitrite concentrations within the method quantification range and to minimize interference from amino acids and bases. The diluted sample (10 mL) was mixed with 0.4 mL color reagent. After 10 min, the solution absorbance at 543 nm was measured, which was proportional to the nitrite concentration in the diluted sample.

Total nitrosamine, the sum of all compounds featuring the *N*-nitroso