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Solubility and thermodynamic modeling of carcinogenic nitrosamines in aqueous amine solvents for CO₂ capture

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Abstract

A better understanding of key fundamental properties of nitrosamines, including their solubility in aqueous amine solvents, is needed to understand and accurately model the vapor-phase emission levels from operating CO₂ capture systems. In this work, the first experimental Henry's volatility coefficient of a nitrosamine was obtained with a novel method using static headspace solid phase micro extraction (SPME) and gas chromatography mass spectrometry (GC/MS). The experimentally determined Henry's volatility coefficient of nitrosopyrrolidine (NPY) was found to be around 0.02 (dimensionless) at 25 °C, and falls in the range of a semi-volatile compound. A linear temperature dependency of the Henry's volatility coefficient can be observed, however additional data is need to verify this trend.

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Keywords: Nitrosamine, Henry's volatility coefficient, SPME, CO₂ capture

1. Main text

The control and capture of carbon dioxide (CO₂) from major industries such as coal burning power plants is considered as the most effective solution in tackling CO₂ induced climate change. Among the various capture approaches, chemical absorption in aqueous amine solvents is currently the most promising option for separating CO₂

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from coal combustion flue gas due to its relatively simple operation, high absorption efficiency, and technological maturity. Solvent degradation is a major economic and environmental factor in using amines for CO₂ capture. Amine solvents will degrade through oxidation and thermal degradation pathways, in addition to reactions with flue gas components, including fly ash, SO_x and NO_x.

Amines, specifically secondary amines can specifically react with NO_x to form a class of secondary degradation products known as nitrosamines [1]. Nitrosamines are a class of carcinogenic compounds previously associated with cigarette smoke, cooked meat and vehicle emissions, but more recently as a disinfectant byproduct formed during chlorination of wastewater [2-3]. Due to the recent rapid development of CO₂ capture systems employing aqueous amine solvents, nitrosamines now represent an emerging environmental contaminant if their emission from operating CO₂ capture systems cannot be better understood and controlled. With the current regulatory push for CO₂ capture technologies, the potential exists for a dramatic increase in environmental emissions of nitrosamines.

The highest health risk to the general population from CO₂ capture facilities has been associated with nitrosamines dispersed to the surrounding ambient air and drinking water, with direct nitrosamines emissions from a CO₂ capture facility having the most important contribution to the increase risk [4]. A recent health risk assessment for nitrosamine emissions from a CO₂ capture facility reported the estimated acceptable air concentrations of several nitrosamines based on a tolerable risk level of one-in one million extra risk at between 0.06 – 0.16 µg/m³ [5]. This report also acknowledged that more research is needed in the areas of nitrosamine emission rates and dispersion to better estimate the potential risks.

A better understanding of key fundamental properties of nitrosamines, including their solubility in aqueous amine solvents, is needed to understand and accurately model the vapor-phase emission levels from operating CO₂ capture systems. Currently, there is very little information available regarding the gas phase concentration of nitrosamine from CO₂ capture facilities and there are no known reports of the vapor-liquid equilibrium (VLE) or thermodynamic data for nitrosamines in aqueous amine solvents. Cousins et al. used an estimated Henry's coefficient to calculate nitrosopiperazine (NPZ) emissions from water wash values obtained at a pilot CO₂ capture system using a 10% piperazine solvent [6]. However, it was noted in this study that the emission values were only an approximation due to the low confidence in the NPZ Henry's coefficient used.

In this work, the experimental Henry's volatility coefficient of a model nitrosamine in a reference aqueous amine solvent was obtained with a novel method using static headspace solid phase micro extraction (SPME) and gas chromatography mass spectrometry (GC/MS) [7].

2. Experimental Methods

2.1. Calculation of Henry's volatility coefficient

The dimensionless Henry's volatility coefficient for component *i*, can be expressed in Eq. 1 as a ratio of the equilibrium concentration in the headspace (*C_{i,HS}*) and liquid (*C_{i,L}*) at a specific temperature.

$$H = \frac{C_{i,HS}}{C_{i,L}} \quad (1)$$

Assuming a closed system with a single volatile compound, in this case a nitrosamine, we can express *H* as in Eq. 2 where *V_{HS}* and *V_L* are the headspace and liquid volumes, and *n_{HS}* and *n_L* represent the number of moles of nitrosamine in the headspace and liquid respectively.

$$\frac{n_{HS}}{n_L} = H \frac{V_{HS}}{V_L} \quad (2)$$

The total number of moles of nitrosamine (n_t) is equal to $n_{HS} + n_L$ allowing Eq. 2 to be rewritten to:

$$n_{HS} = n_L \frac{H(V_{HS}/V_L)}{H(V_{HS}/V_L) + 1} \quad (3)$$

Further modification can be made to Eq. 3 taking into account that the result obtained from gas chromatography (GC) will be peak areas that are proportional to the concentration of component i . The peak area of a component (A) will be proportional to the vapor phase concentration (n_{HS}) and the headspace volume (V_{HS}) allowing Eq. 3 to be rewritten to the following:

$$AV_L = \frac{kn_iH}{H(V_{HS}/V_L) + 1} \quad (4)$$

Experimentally, V_L can be measured and n_t will be held constant. The constant k is proportional to the peak area (A) and number of moles of the analyte. In terms of GC analysis, this is the same as the slope of a calibration curve of detector response versus concentration. The magnitude of k is constant as long as the experimental concentration of the component of interest falls into the region where detector response versus concentration is linear. Given that for this set of experiments the total moles of nitrosamine (n_t) in solution is held constant, Eq. 4 can be further transformed into a linear equation:

$$\frac{1}{AV_L} = \frac{1}{k'} \frac{V_{HS}}{V_L} + \frac{1}{k'H} \quad (5)$$

where $k' = kn_t$. From Eq. 5, when a series of solutions with the same amount of nitrosamine are analyzed, a plot of $1/AV_L$ versus V_{HS}/V_L will yield a straight line where H can be obtained from the slope-intercept ratio [8,9].

2.2. Solid phase microextraction (SPME)

Nitrosopyrrolidine (NPY) was selected as a model nitrosamine compound due to its commercial availability (99%; Sigma-Aldrich, St. Louis MO) and its moderate boiling point (216-218 °C) making it suitable for analysis using GC/MS. Monoethanolamine (MEA) was selected as the reference aqueous amine solvent due to its commercial availability (99%; Alfa Aesar Ward Hill, MA) and common use as a CO₂ capture solvent.

A series of NPY/MEA solutions with different headspace versus liquid volumes (V_{HS}/V_L) were added to vials along with a small stir bar. A solution of NPY (500 mg/L) and MEA (30 wt%) was prepared volumetrically with deionized water. Separate solutions of MEA (30 wt%) and MEA (30 wt%) with CO₂ loading of 0.3 mol CO₂/kg were also prepared. These solutions were combined at different volumetric ratios while keeping the mass of NPY constant in each vial at 500 µg. The volumes of several 20 mL brown glass vials were determined gravimetrically using 18.2 MQ deionized water at 20 °C. The vials were placed in a holder that was lowered into a water bath with a thermocouple controller. NPY headspace extractions were conducted at 25 °C, and several different temperatures (40, 55 and 70 °C) selected to replicate temperature conditions inside an absorber column. Each vial was analyzed in triplicate to reduce extraction uncertainty.

A manual SPME fiber holder and a 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber (Supelco, Bellefonte PA) were used in these experiments as shown in Fig. 1. Initial headspace sampling was conducted between 3 – 30 minutes to determine when SPME fiber equilibrium was achieved. Equilibrium was reached near 15 minutes, therefore a 15 minute SPME sampling time was used for all subsequent experiments. Preliminary analysis concluded that individual vials reached equilibrium between 2-4 hours at the experimental temperatures, therefore all sampling was conducted after allowing the vial to equilibrate for a minimum of 4 hours.

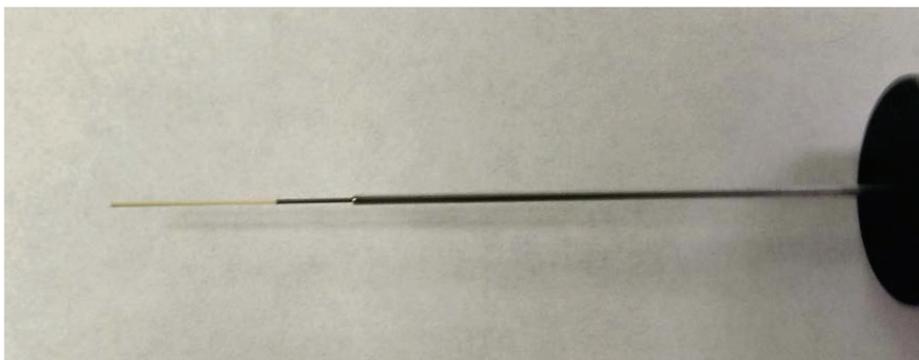


Fig. 1. SPME fiber with PDMS/DVB adsorbant polymer (white/yellow material coating the tip).

2.3. GS/MS analysis

GC/MS analysis was performed with an Agilent 7890A GC with 5975C EI/MSD (Santa Clara, CA). An Agilent DB624 (60 m X 320 μm X 1.8 μm) analytical column and inert (1.38 m x 150 μm x 0 μm) guard column was used with a temperature program of 50 $^{\circ}\text{C}$ for 1 minutes followed by a ramp rate of 15 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$ with a 2 minute hold. The inlet was maintained at 250 $^{\circ}\text{C}$ in splitless mode with ultra-high pure helium (Scott Gross Inc., Lexington KY) at 1.5 mL/min. The MS detector was operated at 70 eV in scan mode from 35-150 m/z. The peak area of NPY was calculated from the ion fragment ratios for NPY (100, 41, 68 m/z).

The SPME fiber was manually inserted into the GC inlet and left for 8 minutes to ensure complete desorption. Preliminary experiments determined that an 8 minute desorption time was sufficient to keep NPY carryover at less than 1%. Additionally, a series of NPY standards were evaluated to verify that the experimental concentration range fell within the linear range of the MS detector.

3. Results and Discussion

Fig. 2 shows a representative plot of $1/AV_L$ versus V_{HS}/V_L at 25 $^{\circ}\text{C}$ (left) and 70 $^{\circ}\text{C}$ (right) for a series of NPY-MEA solutions with constant NPY mass, but different V_{HS}/V_L ratios. The Henry's volatility coefficient for NPY is calculated from the slope/intercept ratio using Equation 5.

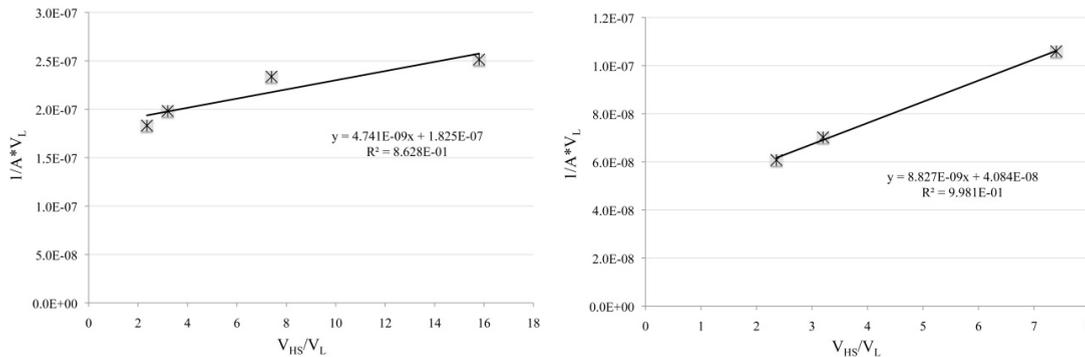


Fig. 2. Plot of $1/AV_L$ versus V_{HS}/V_L at 25 °C (left) and 70 °C (right) used to calculate the Henry’s volatility coefficient for NPY.

Fig. 3 show the plot of $1/AV_L$ versus V_{HS}/V_L at 25 °C for NPY in 30% MEA and in 30% MEA with CO_2 loading at 0.3 mol CO_2 /kg (C/N (α) = 0.3). From this plot it appears that the Henry’s coefficient for NPY in these solutions was not impacted by the CO_2 loading in the solvent. This is an important assessment as a solvent will always have some residual CO_2 loading, especially as it enters the absorber, and will become CO_2 richer as it moves down the absorber column.

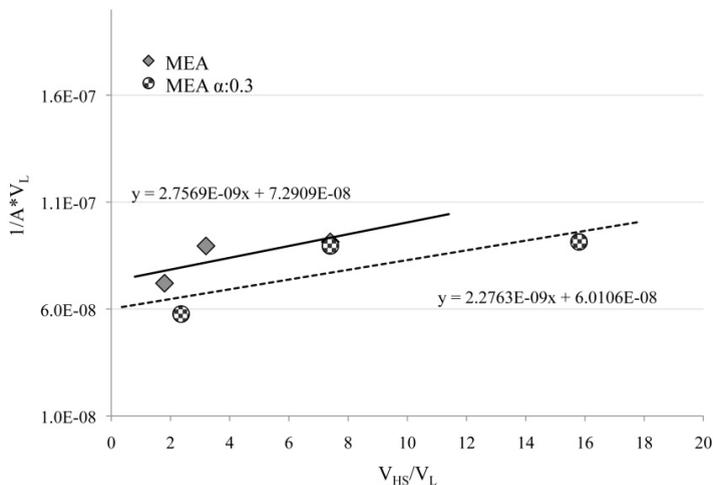


Fig. 3. Plot of $1/AV_L$ versus V_{HS}/V_L at 40 °C in solutions with and without CO_2 loading ($\alpha = 0.3$) used to calculate the Henry’s volatility coefficient for NPY.

Table 1 contains the Henry’s volatility coefficient for NPY calculated in this work. Several data point were repeated yielding a range of values, which is common in experimental determination of Henry’s coefficients [8].

Table 1. Calculated NPY Henry’s Volatility Coefficient.

Temperature (°C)	H (without CO ₂ loading)	H (with CO ₂ loading)
25	0.017 – 0.026	-
40	0.038 – 0.062	0.038 – 0.049
70	0.216	-

Due to the limited availability of Henry’s solubility or volatility coefficients for nitrosamines in the literature, a direct comparison of these results is not possible. However, this data can be put into some perspective by comparing to the Henry’s volatility coefficient of other common organic compounds (Table 2) [7,8,10]. Nitrosopyrrolidine falls between what would be considered volatile compounds such as benzene, and semi-volatile compounds such as toluene and naphthalene.

Table 2. Comparison of Henry’s Volatility Coefficient (dimensionless) for common organic compounds.

Compound	<i>H</i>	Temperature (°C)
Anthracene	5 [10]	25
Benzene	0.21 [8]	25
Toluene	0.225 [8]	25
Nitrosopyrrolidine	0.02 [this work]	25
Naphthalene	0.013-0.018 [7]	25

The temperature dependency of the NPY Henry’s volatility coefficient was also explored by preparing an Arrhenius plot of ln H versus 1/T as presented in Fig. 4. A linear temperature dependency can be observed, although additional data point are needed to better understand the nature of NPY’s Henry’s volatility temperature dependency.

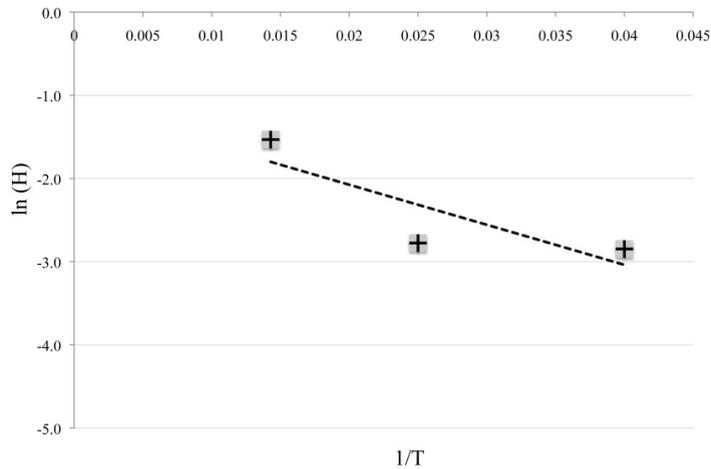


Fig. 4. Arrhenius plot of ln H versus 1/T for NPY.

4. Conclusions

A better understanding of key fundamental properties of nitrosamines, including their solubility in aqueous amine solvents, is needed to understand and accurately model the vapor-phase emission levels from operating CO₂ capture systems. In this work, the first experimental Henry's volatility coefficient of a nitrosamine was obtained with a novel method using static headspace solid phase micro extraction (SPME) and gas chromatography mass spectrometry (GC/MS). The experimentally determined Henry's volatility coefficient of nitrosopyrrolidine (NPY) was found to be around 0.02 (dimensionless) at 25 °C, and falls in the range of a semi-volatile compound. A linear temperature dependency of the Henry's volatility coefficient can be observed, however additional data is need to verify this trend.

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