



1<sup>st</sup> Post Combustion Capture Conference

## Amine volatility in CO<sub>2</sub> capture

Thu Nguyen<sup>a</sup>, Gary Rochelle<sup>a\*</sup>

<sup>a</sup>The University of Texas at Austin, Luminant Carbon Management Program, Department of Chemical Engineering, 1 University Station C0400  
Austin, TX 78712, USA

<sup>b</sup>Second affiliation, Address, City and Postcode, Country

---

Keywords: amine volatility; MEA; PZ; MDEA

---

### Amine Volatility in Binary Amine-H<sub>2</sub>O Systems

The volatility of amines in amine-water was measured using a hot gas FTIR. The amine partial pressures are reported as their respective Henry's constants. At infinite dilution in water, Henry's constants are in the order: Methyl-diethanolamine (MDEA) < 2-Aminoethoxyethanol (DGA<sup>®</sup>) < Piperazine (PZ) < 2-Methyl Piperazine (2-MPZ) < 3-Methylamino Propylamine (MAPA) < Ethylenediamine (EDA) < Monoethanolamine (MEA) < Hexamethylenediamine (HMDA) < 1,2-Diaminopropane (DAP) < 1-Methyl Piperazine (1-MPZ) < 2-Amino-2-Methyl-1-Propanol (AMP) < 1,4-Dimethylpiperazine (DMPZ). The amine Henry's constant at 40 °C is correlated to molecular group contributions:  $\ln H_{40^\circ\text{C}} = 4.19 - 1.65(\text{N}) - 0.21(\text{NH}) - 1.55(\text{R-O-R}) + 0.7(\text{Non Cyclic C-CH}_3) + 2.63(\text{Cyclic N-CH}_3)$ , where the number of each functional group is defined as: N = tertiary nitrogen, NH = secondary amine, R-O-R = ether, Non Cyclic C-CH<sub>3</sub> = C-CH<sub>3</sub> in a straight chained amine, Cyclic N-CH<sub>3</sub> = N-CH<sub>3</sub> in a cyclic amine. Predictions of Henry's constants at 40 °C by the UNIFAC-DMD model in AspenPlus overestimate most measured values up to an order of magnitude except in the case of MEA. Most importantly, it was found that amine volatilities in water don't necessarily track with pure amine boiling points. Additionally, it appears that there is no correlation between aqueous amine volatility and the amine's heat of absorption as estimated per the Gibb's Helmholtz relation  $d(\ln H_{\text{amine}})/d(1/T) = -\Delta H_{\text{abs}}/R$ . The heats of absorption for the amines studied range from 40-85 kJ/mol.

### Amine Volatility in Loaded Amine-CO<sub>2</sub>-H<sub>2</sub>O Systems

Amine volatility is a key criterion used in the screening of new amines for CO<sub>2</sub> capture for a number of reasons. First, volatility losses pose serious environmental risks with the resulting byproducts being potentially more toxic than the parent amines themselves. Amines are found to participate in photo-catalyzed oxidation reactions with NO<sub>x</sub> to form various nitros products, namely nitramines and nitrosamines, with 80% of the latter being reportedly carcinogenic. Second, the make-up costs for spent amines can be quite expensive. Additionally, high volatility

---

\* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .  
E-mail address: author@institute.xxx .

losses also increase the capital cost of the water wash. At the experimental condition representing the top of the absorber (40 °C, nominal lean loading), 8 m PZ solvent has a volatility of ~ 0.78 Pa, which is roughly 3.5 times less volatile than 7 m MEA, the baseline industrial solvent, which has a volatility of as much as 2.7 Pa. Because PZ (a diamine) can participate in multiple reactions with CO<sub>2</sub> as opposed to MEA (a monoamine), PZ volatility is dramatically reduced with loading due to little free amine availability. Looking specifically at the nominal lean loading, because PZ can react with CO<sub>2</sub> in a series of reactions to form PZ carbamate and subsequently to protonated PZ carbamate, there are more than one reaction equilibria competing in the product conversion back to free PZ. MEA, on the other hand, reacts with CO<sub>2</sub> to form only MEA carbamate, thus there is no other equilibria competing with the conversion back to free MEA. The 7 m MDEA/2 m PZ blend is also a choice solvent due to its low volatility. At the experimental condition representing the top of the absorber, MDEA volatility is ~0.76 Pa whereas PZ volatility is ~0.21 Pa. In this blend, MDEA volatility is rather low as this is an inherently nonvolatile amine. Also, its volatility doesn't change dramatically with loading as a consequence of CO<sub>2</sub> reacting preferentially with PZ in the blend as PZ is the stronger base and can form amine carbamates.