



1st Post Combustion Capture Conference

Amines in the Atmosphere: Thermodynamic Properties and Gas/Particle Partitioning

Xinlei Ge¹, Anthony S. Wexler¹, Simon L. Clegg^{1,2*}

¹Air Quality Research Center, University of California, Davis, CA 95616, USA

²School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK

Amines; atmospheric behaviour; sources; gas/particle partitioning; thermodynamic properties; modelling.

1. Introduction and Summary

Amines can be emitted by a wide range of natural and industrial sources – possibly including losses from CO₂ capture systems in the future – and are ubiquitous atmospheric organic bases. Approximately 150 amines and about 30 amino acids have been identified in the atmosphere. We have first of all reviewed the present knowledge of atmospherically relevant amines with respect to their sources, fluxes, and dynamics including gas-phase reactions, gas-to-particle conversion and deposition.⁽¹⁾ Second, we have compiled data for the thermodynamic properties of the amines which control gas/particle partitioning and therefore the removal of amines from the atmosphere by wet deposition.⁽²⁾ Prediction methods for boiling point, liquid vapor pressure, acid dissociation constant and the solubility of the amines in water have been evaluated, and used to estimate values of the equilibrium constants where experimental data are lacking. The partitioning of amines into aqueous atmospheric aerosol particles, fog water, and cloud droplets is strongly dependent upon pH and is greatest for acidic aerosols. For several common amines the tendency to partition to the aerosol phase is similar to or greater than that of ammonia.

2. Amines in the Atmosphere

Amines play a role in the atmosphere that is similar to that of ammonia. They are atmospheric bases so may neutralize the acidity of ubiquitous acids such as sulfuric acid and nitric acid, they are semi-volatile so may occur in both the gas and particle (aerosol, fog water and cloud water) phases, and their major sources include natural and animal feeding operations. Some are highly toxic. Although amines are emitted by a wide range of anthropogenic and natural sources, a new source category may be emerging: carbon sequestration. Amines are thought to be likely compounds for scrubbing CO₂ from flue gas. Current designs recycle the amines, but there is evidence of some loss directly, and via conversion to ammonia in the cycle. For instance, concentrations of amines have been observed in the low ppm levels near the Karsto power plant in Norway, one of the first to employ this technology. Amine loss

* Corresponding author. Tel.: +44-(0)1603-593185; fax: +44-(0)1603-591327.

E-mail address: s.clegg@uea.ac.uk.

not only increases plant operating cost substantially, but it also adds a new source of amines and possibly ammonia to the atmosphere.

Methyl and ethyl amines, including their mono-, di- and tri- forms, are the most common in the atmosphere. Their concentrations are highest near major sources and in confined spaces. For instance, concentrations exceeding 100 mg m^{-3} have been observed near fish stands and values near $15 \text{ } \mu\text{g m}^{-3}$ have been observed near concentrated animal feeding operations.

On a global scale, little is known about the flux of most amines. For methylamines the major emissions strengths, with substantial uncertainty, are animal feeding operations, which contribute about 100 Gg N a^{-1} , oceans which may contribute up to 80 Gg N a^{-1} and biomass burning about 60 Gg N a^{-1} . Sinks include deposition to the surface and chemical reaction. The oceans are thought to be substantial sinks for dimethyl amine via dissolution. Since most of the amines are highly soluble, wet deposition is thought to be a major route for deposition to the surface. Evidence suggests that the wet deposition of amines is dominated by scavenging from the gas phase, with little contribution of particulate amines (amines and aminium salts).

As with most organic compounds in the atmosphere, amines are oxidized by hydroxyl radical, ozone and nitrate radical. Many of their reaction rates have been measured in smog chamber experiments yielding typical lifetimes due to OH attack of the order of hours. Some of the reaction products have low vapor pressures so may contribute to aerosol particle formation, although the accumulation of nitrosamines in the aerosol phase in appreciable amounts is unlikely due to their rapid photolysis under sunlight and their high vapor pressures.

3. Thermodynamic Properties

Henry's Law constants, vapor pressures, activity coefficients, aqueous dissociation constants and solubilities of atmospheric amines (154 amines, 32 amino acids and urea) have been evaluated and compiled. The available measurements are quite sparse, and a number of widely used estimation methods for vapor pressure, dissociation constant and solubility were tested and then used to complete the data set. Vapor pressures of the amines were estimated by combining a measured or predicted boiling point with a predicted enthalpy of vaporization. Our results are presented as tables of values of thermodynamic equilibrium constants, and will also be incorporated into the Extended Aerosol Inorganics Model (*E-AIM*, <http://www.aim.env.uea.ac.uk/aim/aim.php>) to enable gas/aerosol partitioning and other calculations to be carried out on-line.

Simple calculations of gas/aerosol partitioning of amines, as a function of atmospheric liquid water content and pH, confirm that their behaviour is comparable to that of ammonia and that pH is a key property determining partitioning into the aerosol and cloudwater particles and eventual removal from the atmosphere.

4. Acknowledgements

This work was supported by the Electric Power Research Institute.

5. References

1. Xinlei Ge, Anthony S. Wexler, and Simon L. Clegg (2011) Atmospheric amines - Part I. A review, *Atmos. Environ.*, in press.
2. Xinlei Ge, Anthony S. Wexler, and Simon L. Clegg (2011) Atmospheric amines - Part II. Thermodynamic properties and gas/particle partitioning, *Atmos. Environ.*, in press.