Thermodynamic properties and gas/particle partitioning of atmospheric amines

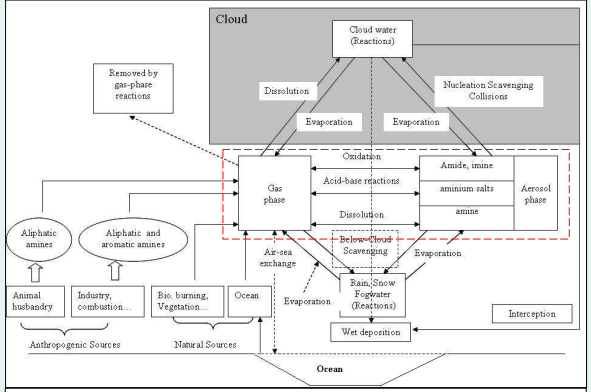
Xinlei Ge[1], Anthony S. Wexler[1], Simon L. Clegg[1,2]
[1]Air Quality Research Center, University of California, Davis, CA95616, USA
[2]School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK
Email: xlge@ucdavis.edu; aswexler@ucdavis.edu; S.Clegg@uea.ac.uk

Abstract

Amines can be emitted into the atmosphere from a variety of sources, and they are also among one of the important groups of organic species in atmospheric aerosols and a rare class of bases. However, relatively little is known about the atmospheric chemistry of amines, and how they may lead to particle formation.

This work presents a thermodynamic study of the atmospheric amines(154 amines, 32 amino acids and urea) with regard to the gas/particle partitioning. The thermodynamic data will be incorporated into E-AIM(http://www.aim.env.uea.ac.uk/aim/aim.php, Wexler and Clegg, 2002) so that researchers can both interpret the results of laboratory experiments involving amines and investigate their probable atmospheric behavior. We also estimated the dissociation constants and their variation with temperature and relative humidity(RH) of aminium salts, such as aminium chloride and nitrates, and their likely competition with ammonium salts on gas/aerosol partitioning.

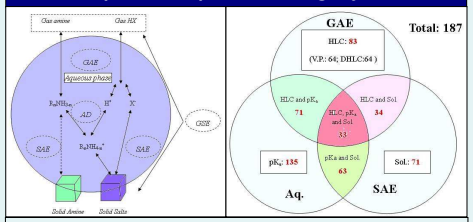
An overview of atmospheric amines



A general overview of the present knowledge finds out that 154 amines, 32 amino acids, and urea have been identified in the atmosphere.

Two pathways contribute to amine gas-to-particle conversion:
dissolution due to their high aqueous solubility and
acid-base neutralizing reactions due to their role as atmospheric bases.

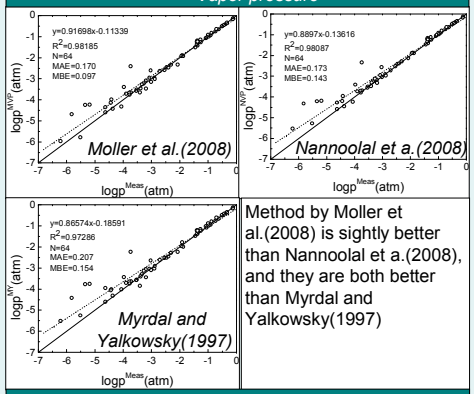
Gas/particle partitioning system



Model system | Required Data availability

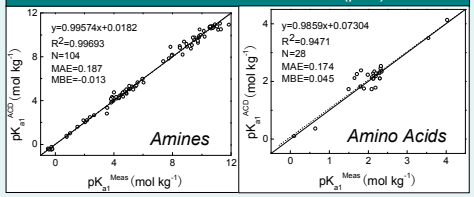
Data evaluation and estimation

Vapor pressure

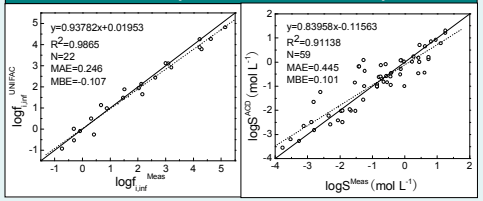


Method by Moller et al.(2008) is sightly better than Nannoolal et a.(2008), and they are both better than Myrdal and Yalkowsky(1997)

Acid dissociation constants(pKa)



Activity coefficients and solubility



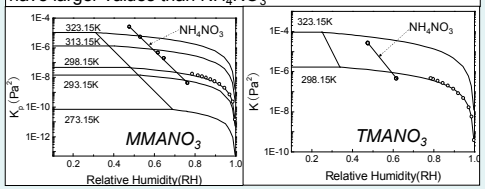
Dissociation constants of aminium salts

$$R_nNH_{4-n}X(p) \leftrightarrow R_nNH_{3-n}(g) + HX(g)$$

$$K_p = p_{R_nNH_{3-n}} \cdot p_{HX}$$

19 chlorides at 298.15K: Chloride of TMA, aniline and N-Methylaniline have larger values than NH_4Cl.

11 nitrates at 273.15-323.15K: Nitrate of TMA and aniline have larger values than NH_4NO_3



References:

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