

# A simplified model to predict partitioning between the vapour and multiple condensed phases in mixed inorganic- organic aerosol particles

D. Topping<sup>1,2</sup>, G. McFiggans<sup>2</sup> and M. Barley<sup>2</sup>

<sup>1</sup>National Centre for Atmospheric Science (NCAS), University of Manchester, Oxford Road, Manchester, UK.

<sup>2</sup>University of Manchester, Oxford Road, Manchester, UK

Keywords: aerosol particles, thermodynamics, .

Presenting author email: david.topping@manchester.ac.uk

## Introduction

Knowledge of the physical state and morphology of internally mixed organic/inorganic aerosol particles is still largely uncertain (Song et al 2012). The wide range of concentrations and properties of organic compounds found within aerosol particles in the atmosphere suggest that liquid-liquid phase separation equilibrium ('LLE') might occur in certain ambient conditions. Predicting the equilibrium composition in multicomponent inorganic-organic aerosol particles using thermodynamic models has remained a challenge. Traditionally the most complex, and seemingly accurate, models rely on minimisation of the Gibbs energy of the system.

Currently available thermodynamic methods that account for partitioning between two liquid phases are computationally expensive and do not account for the vast number of organics expected to contribute to the condensed phase. Whilst empirical parameterisations based on organic:sulphate and O:C ratios have been constrained to specific systems (Bertram et al 2011), there is no general consensus on how to account for LLE across a broad range of scenarios. In this study, we reformulate the problem such that it can be solved using a robust and efficient iterative method and thus derive a generic simplified method for predicting coupled VLE and LLE in atmospheric aerosol particles. Comparisons with more complex benchmark models are made (figure 1) along with a discussion as the wider significance of LLE in relation to additional uncertainties in other properties.

Using the activity coefficient model AIOMFAC (Zuend et al 2008), partitioning coefficients between two liquid phases are derived based on the assumption of a continuum of forces that represent molecules that interact by London Dispersion forces (hydrocarbons) and molecules that interact by dipoles/hydrogen-bonding/electrostatic charges. Organics of atmospheric interest are assumed to form a continuum between H-bonding/dipole interactions at one extreme and purely London Dispersion forces at the other, so all these compounds partition between the two phases (assumed aqueous and hydrocarbon in this study). In this method the composition space is explored to discover the least miscible components (solvents) based on predictions from the AIOMFAC activity coefficient model.

## Results

To test the applicability of the simplified model a set of coupled VLE-LLE partitioning calculations are compared with the results of Zuend et al (2010) for a

system with an ammonium sulphate core and 4 organic compounds are multiple relative humidity (RH) (figure 1). Unrestricted with regards to the number of compounds used within the calculations, we then attempt to assess the potential importance of LLE in ambient aerosol using output from a gas phase degradation model with 2727 compounds. Here we use the results described by Barley et al (2010) in which the Master Chemical Mechanism was used to simulate the gas phase composition of air masses over multiple environments. The potential importance of LLE is discussed in relation to existing uncertainties in the properties of organic components.

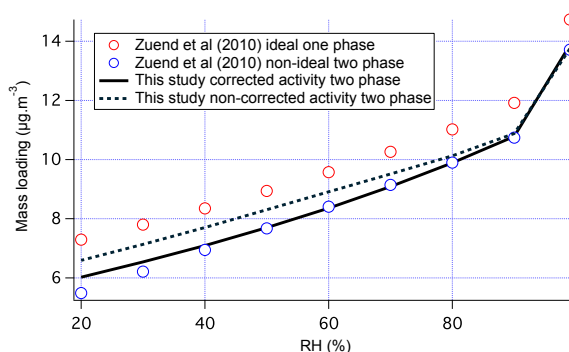


Figure 1. Mass loading of organics as a function of RH. A comparison with a benchmark thermodynamic framework of Zuend et al (2010).

This work was supported by the National Centre for Atmospheric Science (NCAS).

- Barley, M. H., Topping, D., Lowe, D., Utembe, S., and McFiggans, G.: *Atmos. Chem. Phys.*, 11, 13145–13159, doi:10.5194/acp-11-13145-2011, 2011.
- Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., and Zorn, S. R.: *Atmos. Chem. Phys.*, 11, 10995–11006, doi:10.5194/acp-11-10995-2011, 2011.
- Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: *Atmos. Chem. Phys.*, 12, 2691–2712, doi:10.5194/acp-12-2691-2012, 2012.
- Zuend, A., Marcolli, C., Luo, B. P., and Peter, T.: *Atmos. Chem. Phys.*, 8, 4559–4593, doi:10.5194/acp-8-4559-2008, 2008.
- Zuend, A., Marcolli, C., Peter, T., and Seinfeld, J. H.: *Atmos. Chem. Phys.*, 10, 7795–7820, doi:10.5194/acp-10-7795-2010, 2010.