

Connecting the solubility and hygroscopic behavior of complex organic aerosols using solubility distributions

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Introduction

Organic aerosol particles often consist of thousands of compounds with different properties. One of these properties is solubility, which affects the hygroscopic growth and CCN activation of the organic particles. Here we investigate the water-interactions of complex organic aerosols accounting for the distribution of solubilities present in these mixtures 1) through a theoretical study exploring the sensitivity of CCN activation to the solubility distribution; 2) through comparison of theoretical predictions utilizing solubility distributions to experimental data collected from the field and laboratory for realistic atmospheric organic mixtures (see e.g. Pajunoja et al., 2015).

Methods

In all the calculations we considered a population of spherical aerosol particles consisting of an internal mixture of organic compounds. When exposed to water vapor, these particles were assumed to grow reaching a thermodynamic equilibrium between the water vapor and the particle phase. The composition of the organic and aqueous phases was determined on one hand by the equilibrium between the aqueous phase and water vapor, and on the other hand by the equilibrium of the aqueous phase with the organic insoluble phase. We modelled the mixture with n surrogate compounds with varying solubilities. Varying the range and shape of the solubility distribution, as well as the number of components n in the distribution. We also assumed two different kinds of interactions between the organic compounds in the insoluble phase: 1) ideal mixture, where organics limit each other's dissolution; 2) unity activity, where organics behave as pure compounds and do not influence each other's dissolution.

For the CCN activation study, the critical supersaturations and the dissolution behavior at the point of CCN activation were calculated utilizing the Köhler theory for all organic mixtures (denoted here as the "full model"). For the comparisons to the experimental data, similar calculations were conducted for idealized mixtures representing isoprene and monoterpene-derived Secondary Organic Aerosol (SOA).

Results and Discussion

Figure 1 shows the comparisons of the full model predictions to the commonly-used three simplified solubility models: 1) assuming complete dissolution of all compounds; 2) treating the organic mixture solubility with the hygroscopicity parameter κ and 3) assuming a fixed soluble fraction ε for each mixture. The comparison between the full model and the complete dissolution assumption demonstrated a systematic under-prediction (up to 40%) of the activation diameter, while the κ and ε -based solubility models were generally within 10% (in most cases within 5%) of the activation diameter predicted using the full solubility distribution representation, see Fig 1. The ε and κ values were found to correspond to the fraction of material with solubilities larger than a given threshold solubility c_t . The median threshold for the ideal mixture assumption was 10 g L^{-1} , with most of the c_t values falling between 1 and 100 g L^{-1} . For the unity organic activity assumption this median threshold was 1 g L^{-1} , with most of the c_t values falling between 0.1 and 10 g L^{-1} .

Our preliminary results also indicate a good agreement between the modeled and experimental hygroscopicity and CCN activation of realistic ambient organic aerosols, given that the solubility and potential adsorption effects at low RHs are accounted for (Pajunoja et al., 2015).

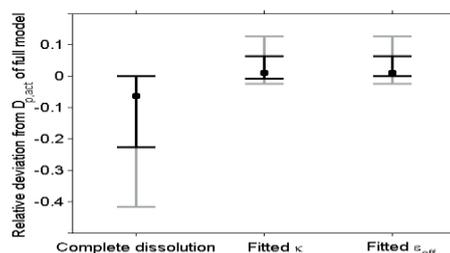


Figure 1. The performance of the simplified models in predicting the activation diameter as compared with the full model. The black bars depict the 25 and 75 percentiles and the gray bars the 10 and 90 percentiles.

Pajunoja, A., Lambe, A.T., Hakala, J., Rastak, N., Cummings, M.J., Brogan, J.F., Hao, L., Paramonov, M., Hong, J., Malila, J., Romakkaniemi, S., Lehtinen, K., Laaksonen, A., Onasch, T.B., Donahue, N.M., Riipinen, I., Davidovits, P., Worsnop, D.R., Petäjä, T., Virtanen, A. (2015) *Geophys. Res. Lett.* (In review process).