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Atmospheric
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Discussions

Interactive comment on “Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols” *by* A. Zuend et al.

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The authors would like to thank reviewer #1 for the consideration of the manuscript and valuable queries and comments.
We have addressed the reviewer’s general and specific points below.

General points

“The authors restrict the calculations to two separate liquid phases. This is understandable given the complexity of the calculations. However, would this assumption hold for more complex organic systems which a broader range of functionality, polarity etc? In essence, can the conclusions derived in this study really be generalised to interpret much more complex systems, such as smog chamber ensemble studies?”

The upper limit for the number of different liquid phases that might form at thermodynamic equilibrium is described by Gibbs’ phase rule. For example, a closed gas-particle system containing 10 components at a given temperature could potentially form up to 10 different liquid phases. However, experimental studies show that multicomponent organic-inorganic mixtures most often form up to two and in rare cases three different liquid phases. More than two liquid phases typically only exist in a very narrow composition range. The number of liquid aerosol phases that form at equilibrium is mainly determined by the range of hydrophilicities (polarity) of the different organic compounds and the aerosol water content. With a hydrophilic, aqueous electrolyte-rich phase and a much less hydrophilic organic-rich phase, either one of the two liquid phases offers sufficient affinity for the majority of condensable organic compounds, rendering an additional liquid phase unnecessary. Some organic compounds show significant affinity for both phases, reflected in their liquid-liquid phase distribution. Concerning the effects on gas/particle partitioning in the rare cases where more than two liquid phases would coexist in a certain composition range, the effect of only assuming two liquid phases will presumably be much smaller than the error when liquid-liquid phase separation is not considered at all. Thus, we consider a maximum of two liquid phases to be a valid and reasonable assumption for the majority of aerosol mixtures. However, depending on temperature and RH, in complex aerosol systems it might be possible that besides the liquid phases several solid inorganic and/or organic phases exist. In the present calculations, the formation of solids was suppressed, allowing supersaturated solutions at lower RH. In future gas/particle partitioning studies, it might be of more interest to consider effects due to the formation of solids instead of extending the model to allow more than two liquid phases.

"Do the authors think that the interfacial energy between separate phases in actual aerosol particles might influence overall gibbs energy of the system to alter the generalised conclusions reported here? There have been few studies analysing the potential sensitivity of size dependent deliquescence, for example, to interfacial energies."

The change in the total interfacial energy from gas-liquid and liquid-liquid interfaces due to a liquid-liquid phase separation is typically a positive contribution to the system's overall Gibbs energy. Therefore, decreasing RH at constant dry composition of a bulk particle, at a critical RH, a one-phase bulk solution becomes metastable/unstable and subsequently undergoes phase separation, while a smaller particle with a higher surface/volume ratio will remain stable as a one-phase solution at this critical RH due to the higher interfacial energy barrier (on a per mol solution basis). However, further decreasing RH will eventually lead to a phase separation in small particles as well. Hence, we would like to know the difference in critical RH that is required to induce a phase separation in tiny particles. Russell and Ming (2002) studied the effect of particle size and related surface tensions (interfacial energies) on the deliquescence relative humidity (DRH) for initial dry particle diameters ranging from 8 to 100 nm. For sodium chloride particles of 15 nm dry diameter, they find an increase in DRH by 8 % as compared to a large particle (bulk solution). For an initial particle diameter of 50 nm the increase in DRH is 2.5 % and for particles with dry diameters of 100 nm and above, the change in DRH is negligible. Since the particle size effects on DRH and on the critical RH, at which a liquid-liquid phase separation occurs, are both related to changes in the total interfacial energy, as a first order approximation, we can assume the size effects to be of similar magnitude. This means that for aerosol particles with diameters larger than 100 nm, liquid-liquid phase separations will occur

at almost the same RH as in corresponding bulk solutions. Particles of sizes smaller than 100 nm (diameter) will suppress a liquid-liquid phase separation by up to a few % in RH. However, for particles of diameters < 100 nm, the Kelvin effect on gas/particle partitioning will become important too. Thus, regarding particle size effects and considering that particles of diameters > 100 nm account for most of the aerosol mass, the general conclusions of the article will remain the same for actual ambient aerosols.

Specific points

"In section 2.4.2 the authors mention how a specific system may not be perfectly represented within a group contribution method which has been constrained to a specific subset of organic functionality. This has been found in simpler studies using updated parameters within the UNIFAC framework. Given the many combinations of functional groups which would require fitting, do the authors think that there is ultimately a level of accuracy beyond which model predictions will never be attainable given restrictions in bulk analytical techniques (i.e. solubility, evaporation etc). Whilst this is a rather philosophical question, it is an interesting discussion nonetheless."

Group contribution methods as used in UNIFAC and AIOMFAC are based on semi-empirical expressions for the calculation of activity coefficients. These models therefore rely on experimental data to estimate model parameters accounting for non-ideal interactions between different organic functional groups, water, and inorganic ions. In an ideal scenario, in which experimental data for different organic-inorganic mixtures containing all functional groups and ions of interest are abundantly available, accurate, and well distributed over a range of different molecular structures covering monofunctional and multifunctional compounds, the level of accuracy of model predictions would mainly depend on the flexibility of the model expressions to describe all experimentally found mixture behaviour. Computational efficiency versus model accuracy (model complexity) would then constitute the main trade-off. In reality, measurements are not perfectly accurate, experimental data is only available for a subset of required mixtures, biased towards monofunctional, industrially relevant mixtures/components, and group-contribution models have limited flexibility and usually neglect potentially different mixing behaviour of structural isomers. Therefore, there is certainly a practical level of accuracy beyond which activity coefficient model development and model predictions will not be possible in the next couple of years. However, concerning gas/particle partitioning calculations, uncertainties related to the use of vapour pressure estimation methods and with respect to the actual aerosol composition outweigh the limited accuracy of group contribution models. For the ongoing development of the AIOMFAC model to include further functional groups and their interactions with inorganic ions, new experimental data is highly appreciated.

References

Russell, L. M. and Ming, Y.: Deliquescence of small particles, J. Chem. Phys., 116, 311–321, doi:10.1063/1.1420727, 2002.

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