Aerosol particles and cloud droplets affect the radiation balance of the Earth significantly, and at the moment, the uncertainty in predicting future climate is partly due to climate models not being able to precisely capture the behaviour of the aerosol particles or their activation into cloud droplets. This is related, among other things, to the lack of knowledge of physical and chemical properties of aerosol particles and especially to the organic fraction of particles.

There are a large number of different organic compounds in the atmosphere. Despite the many studies of the thermodynamic properties of these organics we still lack a complete characterization of their physico-chemical properties. Dicarboxylic acids are one group of water soluble organic compounds typically found in atmospheric aerosol particles. Studies so far have focused on saturation vapour pressures of pure compounds (Zardini et al., 2006; Riipinen et al., 2006) but little is known about their evaporative behaviour in multi-component mixtures. In this study, the effect of inorganic compounds (sodium chloride and ammonium sulphate) on evaporation of an organic component (succinic acid, a dicarboxylic acid) from aqueous solution droplets is studied and the existing models for calculating activity coefficients for succinic acid are tested.

METHODS

The evaporation rates of solution droplets were measured using a Tandem Differential Mobility Analyzer (TDMA) system modified to study sub-cooled droplets, and coupled with a 3.5 m long laminar flow tube (Koponen et al., 2007). Briefly, a monodisperse droplet population is selected with a DMA and let to the flow-tube where the droplets evaporate and their size change is measured with a Scanning Mobility Particle Sizer (SMPS). The flow tube provides residence times of up to several minutes. The experiments were performed atomizing droplets from two kinds of solutions: succinic acid – sodium chloride – water and succinic acid – ammonium sulphate – water. In the latter case the SMPS measurements were accompanied by an Aerosol Mass Spectrometer (AMS) to monitor the temporal evolution of the chemical composition of the droplets.
The observed change in particle size is compared to that predicted by a theoretical evaporation model based on the mass transport from the droplet. In this model, the inorganic component is assumed to stay in the liquid phase, and the reduction in the particle size is due to evaporation of water and succinic acid. Water is assumed to be equilibrated with the droplet and its partitioning between vapour and particle phase is calculated using the Extended Aerosol Inorganic Model, E-AIM, (www.aim.env.uea.ac.uk, see references therein). E-AIM is used also to calculate the activity coefficient of succinic acid as a function of droplet composition. Due to the long time scale of the evaporation and low number concentration of particles the temperature of the particles and the gas in the flow tube are assumed to be equal and to stay constant. In the evaporation model time step of 1 ms is used and the amount of water in liquid phase and activity coefficients are updated from E-AIM with 5 s time intervals. E-AIM is used with formation of solid phase turned off, and the dissociation of succinic acid is not considered in the evaporation model. Physico-chemical properties of succinic acid used in the evaporation model can be found from previous publications (Koponen et al. 2007; Riipinen et al. 2006; and references therein). Density of the solution is calculated as a mass fraction weighted average of binary aqueous solution densities.

RESULTS

Figure 1 presents a typical result in the case of droplets consisting of succinic acid – sodium chloride – water solution. In general the model predicts the evaporation fairly well. However, when organic fraction in the droplets is small the model overpredicts the evaporation which might suggest that the inorganic compound lowers the activity coefficient of the organic compound even more than predicted by the E-AIM model. For the droplets consisting of succinic acid, sodium chloride and water three equations for succinic acid activity coefficient were tested from E-AIM: Redlich-Kister, UNIFAC with corrections by Peng et al. (2001) and Raoult’s law. All the three gave similar results. In the case of figure 1 Redlich-Kister equation was used.

![Figure 1. Comparison of measured and modelled evaporation rates of droplets consisting of succinic acid, sodium chloride and water.](image)

Figure 2 presents two examples of preliminary results comparing simulated and measured droplet diameters in the case of succinic acid – ammonium sulphate – water droplets. In most of the cases with ammonium sulphate as the inorganic compound the activity coefficients of succinic acid calculated with different methods resulted in significant differences in predicted evaporation rate. In the case of figure 2, as well as in the most of the cases, the UNIFAC parameterization for activity coefficient with modifications by Peng et al. (2001) seems to work better than Redlich-Kister equation. The general difference between model prediction and measurement is like in the case of sodium chloride as the inorganic compound. However, for the droplets containing ammonium sulphate the evaporation rate predicted by the model seems to be in the beginning of the evaporation typically lower than the one
observed in the measurements. Overall, compatibility of the modelled with measured evaporation rates is weaker in the case of droplets containing ammonium sulphate.

Figure 2. Comparison of measured and modelled evaporation rates of droplets consisting of succinic acid, ammonium sulphate and water. In model simulations two activity coefficient equations from E-AIM were used: Redlich-Kister (R-K) equation and UNIFAC parameterization with Peng et al. (2001) modifications.

CONCLUSIONS

Modelled and measured evaporation rates of ternary aqueous solution droplets containing an inorganic compound and succinic acid as an organic compound were compared and validity of activity coefficient models were tested. In general, the model was able to predict the evaporation reasonable well. For droplets containing sodium chloride as the inorganic compound all three activity coefficient models gave similar evaporation rates, whereas for droplets containing ammonium sulphate changing the activity coefficient model resulted in significant difference in modelled evaporation rate and the UNIFAC parameterization with Peng et al. (2001) corrections agreed best with the measurements. In both cases, model overpredicted the evaporation rate when large fraction of succinic acid had evaporated. This might suggest that the inorganic compound lowers the activity coefficient of succinic acid more than predicted by E-AIM model. On the other hand, a fraction of succinic acid might evaporate already before the droplets arrive in the flow tube. In this case the organic mole fraction used as an input parameter would be too large which is bound to cause discrepancy between the model and the measurement. Without exact information on the composition of the droplets it is difficult to say whether this is the case, and this question will be addressed in the future when analysing measurements performed using succinic acid – ammonium sulphate – water droplets during which also the AMS was measuring.

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