



Temperature dependency of activity coefficients in Organic aerosols.

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Earth's radiative budget and atmospheric chemistry are influenced by the aerosol composition, concentration and physical state. Organic aerosols are expected to be present in the liquid state and to retain water even at low relative humidity because the very large number of organic compounds depresses the temperature at which solids form (Marcolli et al., 2004), while inorganic salts dominate the water uptake at high relative humidity. Thus, a liquid aqueous phase would be nearly always present, affecting the overall concentration and the aqueous phase reaction rates. Semi-volatile organic and inorganic aerosol species partition between the gas and aerosol particle phases to maintain thermodynamic equilibrium. The partitioning of semi-volatile organic species between the gas and the particle phase, water content and the phase state of the particles can be calculated when the vapor pressures and the activities of the involved species are known. To study the hygroscopicity and phase equilibria of mixed aerosol particles we use the AIOMFAC group contribution model developed by Zuend et al. (2008). This model is able to calculate activity coefficients covering inorganic, organic, and organic-inorganic interactions in aqueous solutions over a wide composition range. It includes the semi-empirical group contribution model UNIFAC to calculate activity coefficients of organic compounds. The original UNIFAC method (Hansen et al., 1991) was developed mainly for the prediction of vapor-liquid equilibria (VLE) and azeotropic data of small organic molecules. However, for applications to the atmosphere, a good description of large multifunctional organic compounds at ambient to low temperatures are needed. If the temperature dependence of the activity coefficients is neglected, errors on the order of 10-15 % result for a_w at the homogeneous freezing temperature. Therefore, we intend to further develop UNIFAC to describe better organic molecules and temperatures observed in the troposphere.

Experimental data such as vapor-liquid (VLE), liquid-liquid (LLE), and solid-liquid equilibria (SLE) are used to determine the model parameters for the functional groups that are of special interest to atmospheric aerosols. Temperature dependency studies are carried out for alcohols/polyols and organic acids covering the $-OH$ and $-COOH$ functional groups. In case of alcohols/polyols, we base our temperature dependent parameterization on the modified UNIFAC parameters given by Marcolli et al. (2005) and in case of monocarboxylic and dicarboxylic acids we use the original UNIFAC parameterization and the Peng parameterizations (Peng et al., 2001), respectively.

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