Water uptake by aerosol: Water activity in supersaturated potassium solutions and deliquescence as a function of temperature

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Abstract

Atmospheric aerosol models often calculate water uptake by particles based on information on salt deliquescence and electrolyte mixing rules. Therefore improvements in deliquescence predictions and in the water-activity relations used in mixing rules can improve estimates of size distributions. The primary goals of this work are to derive equations for the variation in the mutual deliquescence relative humidity (MDRH) with temperature (T) for a particle containing an arbitrary number of hydrated and anhydrous salts and to extend the range of validity of water–activity relations reported for binary solutions of KNO_3, KCl, KBr, and K_2SO_4 to greater supersaturations. Equations for MDRH(T) are derived based on the equilibrium conditions that define deliquescence and the Gibbs-Duhem relation. MDRH is calculated from solubility data and the ZSR mixing rule to generate reference values for the equations and to evaluate their reliability. The ZSR mixing rule is also used to predict concentrations of KNO_3, KCl, KBr, and K_2SO_4 in highly supersaturated binary solutions. Polynomial fits are presented that relate water activity to concentration for these solutions. The deliquescence equations derived here predict MDRH(T) for hydrate systems with sufficient accuracy for temperature excursions of about 25 K. MDRH(T) usually follows the trend of DRH(T) for the most soluble salt in the system, while the temperature dependence of saturation concentration can be neglected for some salt systems. A linear temperature dependence for saturation concentration appears necessary to capture MDRH(T) for systems containing $Ca(NO_3)_2 \cdot 4H_2O$ and $CaCl_2 \cdot 6H_2O$. Consideration of deliquescence for a representative sea-salt system indicates that minor hydrated components have an important influence on the uptake of water by sea-salt particles and should be considered in equilibrium aerosol models. Results of this study improve estimates of water uptake by atmospheric particles containing hydrates and potassium salts.

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1. Introduction

Atmospheric particles are often multicomponent systems of salts with some of the salts existing as hydrates. Many of the particle components are hygroscopic and form aqueous solutions by acquiring gas-phase water from humid environments. The uptake of water by hygroscopic constituents of airborne particles significantly alters particle reactivity, radiative properties, and cloud-droplet nucleation efficiency. Aerosol models developed for atmospheric applications generally determine if water is present in a particle using information on salt deliquescence and calculate aerosol water content using electrolyte mixing rules (e.g., Zaveri et al., 2005). Realistic predictions of aerosol water content by these models are critical for calculating the aerosol size and composition distributions used in estimating the influence of atmospheric particles on climate and health.

The deliquescence relative humidity (DRH) of a pure crystalline salt is defined as the relative humidity (RH) at which the crystal acquires gas-phase water to form an electrolyte solution. For salts common in atmospheric particles, the equilibrium phase transition of deliquescence is usually spontaneous (Tang, 1976). In the case of multicomponent systems, the mutual DRH (MDRH) is defined as the RH at which the salt mixture first acquires gas-phase water on exposure to increasing RH and is generally less than the DRHs of all component salts (Wexler and Seinfeld, 1991). At its MDRH, a multicomponent particle consists of the eutonic solution and possibly one or more solid phases. Measurements of the DRH of common salts are readily available at 298 K, and so research has focused on predicting how DRH varies with temperature (T). Stelson and Seinfeld (1982) estimated $DRH(T)$ for NH_4NO_3 based on experimental observations. Wexler and Seinfeld (1991) derived an expression for $DRH(T)$ that is applicable to anhydrous salts in general. Tang and Munkelwitz (1993; 1994) improved this expression by accounting for the temperature dependence of saturation concentrations and reported an equation for $MDRH(T)$ for particles composed of two anhydrous salts. Nenes et al. (1998) reported an $MDRH(T)$ expression for an arbitrary number of anhydrous salts under the assumption of constant saturation concentrations and latent heats. Recently, Kelly and Wexler (2005) derived an expression for $DRH(T)$ for hydrated compounds and demonstrated that $DRH(T)$ can be considerably different for hydrated and anhydrous forms of a given salt. Despite the attention given to the temperature dependence of deliquescence, a general expression applicable to atmospheric particles containing an arbitrary number of hydrated and anhydrous salts is not yet available. Furthermore, measurements of MDRH are scarce, and the deliquescence equations require information on MDRH at a reference temperature (e.g., Tang and Munkelwitz, 1994; Nenes et al., 1998).

Electrolyte mixing rules estimate thermodynamic properties of multicomponent solutions based those of the binary solutions (one salt plus water) of the individual components. Numerous mixing rules have been proposed, and one of the most widely used is the ZSR (Zdanovskii, 1948; Stokes and Robinson, 1966) rule. This model is sufficiently accurate for atmospheric applications when binary solution data are available (Cohen et al., 1987b; Chan et al., 1992; Chan et al., 1997; Tang, 1997) and is attractive because of its simplicity. The water content of a multicomponent solution droplet can be calculated from the ZSR rule if the concentrations of the components in the mixture as well as the concentrations of the components in their respective binary solutions are known at the water activity of the mixture. Often the water activity of a multicomponent solution corresponds to supersaturated conditions for the binary solutions of the components. In these situations, information on electrolyte concentrations in supersaturated binary solutions is required to predict aerosol water content using the ZSR model. Water activity measurements with the electrodynamic balance (EDB) have provided data for supersaturated binary solutions that greatly enhance the utility of mixing rules for predicting aerosol water content (e.g., Cohen et al., 1987a; Chan et al., 1992). However, water activity information for binary solutions at supersaturations even greater than those attained in EDB studies is desirable in connection with using mixing rules for aerosol systems.

Sangster et al. (1973) presented a method whereby water activity measurements for a ternary solution (two salts plus water) are used to predict a component's concentration in a supersaturated binary solution. The method essentially uses the ZSR mixing rule in reverse and can be applied when the concentrations of both electrolytes in a ternary solution and the concentration of one electrolyte in its binary solution are known at the water activity of the ternary solution. Chan and Ha (1999) used the method of Sangster et al. (1973) in conjunction with EDB measurements to calculate the binary solution concentrations of a number of atmospherically important compounds deep into their supersaturated regimes. However, potassium salts were