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The deliquescence behaviour, solubilities, and densities of aqueous solutions of five methyl- and ethyl-aminium sulphate salts

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HIGHLIGHTS

- ► Densities of aqueous solutions of five aminium sulphate salts have been determined.
- ► Water uptake of five alkyl aminium sulphates as f(*RH*) is similar to $(NH_4)_2SO_4$.
- ► Deliquescence properties of mixtures with $(NH_4)_2SO_4$ agree with model calculations.
- ► The treatment of the salts by *E-AIM* (www.aim.env.uea.ac.uk/aim/aim.php) is described.

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ABSTRACT

We report measured solubilities of five aminium (i.e., monomethyl, dimethyl, trimethyl, diethyl, and triethyl) sulphate salts in water at 24 °C, and the densities of their aqueous solutions. Using these results, we have converted hygroscopic growth factors determined by Qiu and Zhang (Environ. Sci. Technol. 2012, 46, 4474–4480) to a moles of water per mole of solute basis, and obtained the relationships between concentration and equilibrium relative humidity (water activity) for solutions of the five salts. The results are compared with values predicted using the Extended Aerosol Inorganics Model (*E-AIM*) of Clegg and co-workers (J. Geophys. Res. 2002, 107, D14, Art. No. 4207). It is assumed in this model that ion and water activities in the solutions are the same as those for aqueous $(NH_4)_2SO_4$ at the same molality. The experimental and modelled growth factors agree well in all cases, within the uncertainties of the data, which supports this assumption. Equations for the apparent molar volumes of the aminium sulphate salts in aqueous solutions are presented (based upon the measured densities and literature data), and also activity products of the salts in saturated aqueous solutions (based upon the measured solubilities and assumption of similarity with $(NH_4)_2SO_4$). Simulations of the deliquescence curves of 1:1 and 1:9 mass ratio mixtures of monomethyl and dimethyl aminium sulphate with $(NH_4)_2SO_4$ are shown to agree well with the measurements. The treatment of amines and aminium salts in the *E-AIM* model is described.

1. Introduction

Amines found in the atmosphere are generated from both biogenic and anthropogenic sources (Ge et al., 2011a). Like ammonia, they are bases, and have been detected in atmospheric aerosol particles (e.g., Rehbein et al., 2011; Huang et al., 2012). Amines may also contribute to the nucleation and growth of new particles, as predicted in several theoretical studies (e.g., Loukonen et al., 2010; Nadykto et al., 2011; DePalma et al., 2012), and observed in field and laboratory investigations (Berndt et al., 2010; Smith et al., 2010; Wang et al., 2010a; Erupe et al., 2011; Zhao et al., 2011; Paasonen et al., 2012; Yu et al., 2012; Zhang et al., 2012; Qiu and Zhang, 2013). Because of their strong basicity, they can engage in aerosol-phase reactions, including neutralization of sulphuric acid (Wang et al., 2010b) and ammonium bisulphate and the replacement of ammonium with amine (aminium) cations (Bzdek et al., 2010, 2011; Qiu et al., 2011; Chan and Chan, 2011; Liu et al.,

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2012). Amines are of interest as potential reactants in processes to sequester CO_2 generated by power plants (Nielsen et al., 2012).

The dissolution of amines in acidic solutions results in the formation of aminium ions, in the same way as the neutralization of NH_3 yields the ammonium ion. For a simple primary amine the reaction is $RNH_2(aq) + H^+(aq) \leftrightarrow RNH_3^+(aq)$ (Ge et al., 2011b), where R represents an alkyl group. There are measurements of osmotic and activity coefficients of solutions of some aminium chloride and nitrate salts at 25 °C, which could be used to develop thermodynamic models of gas/liquid/solid partitioning involving amines and their salts at this temperature, but no thermal measurements that would allow activities to be calculated at other temperatures. There appear to be no data of either kind for solutions of aminium sulphates. Solubilities in mixed salt systems at 20 °C containing triethylaminium sulphate, and triethylaminium chloride, have been measured at 20 °C by Volkov et al. (1982), and Volkov and Sosnina (1973), respectively. Ge et al. (2011b) have reviewed the available thermodynamic information relating to gas/liquid/solid partitioning for amines and their salts, and incorporated some of the results into the Extended Aerosol Inorganics Model (*E-AIM*) of Clegg and co-workers (e.g., Wexler and Clegg, 2002, and references therein; and http://www.aim.env.uea.ac.uk/aim/aim.php). In the model it has been necessary to assume, because of the lack of data, that ion and water activities in aminium chloride, nitrate and sulphate solutions (and the model parameters for interactions between these species) are the same as those of the corresponding ammonium salts at all temperatures and concentrations. There is a need for data both to test these assumptions and, in the future, to develop thermodynamic models of systems containing amines that are based upon the measured properties of the compounds and their mixtures with water and other components of the atmospheric aerosol.

Recently, Qiu and Zhang (2012) have determined growth factors, as a function of equilibrium relative humidity at 24 °C, of aerosols of the following aminium sulphates: monomethyl (MMAS, CAS registry no. 33689-83-7), dimethyl (DMAS, 21249-13-8), trimethyl (TMAS, 54272-30-9), diethyl (DEAS, 26292-53-5), and triethyl (TEAS, 2399-73-7). They also measured growth factors of mixtures of two of the salts with ammonium sulphate, and observed the formation of both types of solid. In this work, new measurements of densities of aqueous solutions of the aminium sulphates are presented, and also the solubilities of the sulphate salts in water at room temperature. Using these data, we convert the results of Qiu and Zhang (2012) from a volume to a molar basis and obtain the relationships between concentration and equilibrium relative humidity (water activity) for the five salts. We also test the assumption of similarity with aqueous $(NH_4)_2SO_4$ in two ways: first, by comparing the measured water uptake of the aminium sulphates with that predicted using the *E-AIM* model, and second, by comparing measured and calculated solid/liquid equilibrium and hygroscopic growth factors for systems containing both $(NH_4)_2SO_4$ and MMAS or DMAS.

2. Experiments

Sulphuric acid (98 wt %), diethylamine (DEA, >99%), triethylamine (TEA, >99%), and the 40.0% aqueous solutions of monomethylamine (MMA), dimethylamine (DMA), and trimethylamine were purchased from Sigma–Aldrich and used without further purification. All of the aminium sulphate salts were prepared using a similar method. For example, to prepare DMAS the 98% sulphuric acid solution was diluted to 39.8 wt % with deionized water (18 mΩ cm). A mass of 13.63 g of 40.0 wt % DMA stock solution (containing 0.121 mol of the amine) was placed in a 50 mL round-bottom flask which was then immersed in an ice bath. A total of 14.94 g of 39.8 wt % sulphuric acid solution (containing 0.606 mol of acid) was then added slowly to the flask, with stirring, to neutralize all the amine. The final solution was allowed to warm up, and was kept at room temperature for another 20 min, before the water was removed under vacuum at 60 °C. The preparation procedure was performed twice to accumulate enough DMAS solid for solubility and density measurements.

The solubilities of the aminium sulphates in water at 24 °C were measured next, followed by the densities of their aqueous solutions over a range of concentrations. Again, using DMAS as an example, a known mass of DMAS solid (18.256 g) was transferred to a flask and small amounts of water were added (up to a total of 2.400 g in this case) until a uniform solution was formed. Between the additions of water, the content of the flask was sonicated to ensure thorough mixing. The concentration of this uniform solution is reported as that of the saturated solution, C_s. The aliquots of water added in the mixing procedure were approximately 0.01 g, which implies an uncertainty of about 0.25 wt% in C_s. Solutions containing DMAS at a series of lower concentrations (to about 10 wt%) were prepared by diluting known masses of saturated DMAS aqueous solution with deionized water. The density of each DMAS solution was determined by weighing the mass of the solution present in a volumetric flask at least three times, and then dividing the mass by the volume. The average is reported as the density of the solution. All densities were measured at 24 °C.

3. Densities and apparent molar volumes

The measured densities ρ (g cm^{-3}) are presented in Table 1. They are related to the apparent molar volumes of the solutes V^ϕ (cm^3 mol^{-1}) by the equations:

$$V^\phi = (M_S/\rho) - [(1-x_s)/x_s]18.0152(1/\rho_w - 1/\rho) \qquad (1a)$$

$$V^\phi = (M_S/\rho) - (1000/m)(1/\rho_w - 1/\rho) \qquad (1b)$$

where M_S (g mol^{-1}) is the molar mass of the solute, x_s is its mole fraction in solution, m (mol kg^{-1}) is the molality of the solute and 18.0152 g is the molar mass of pure water. The mole fraction x_s is equal to $n_s/(n_s + n_w)$ where n is the number of moles of solute (s) or water (w). Symbol ρ_w represents the density of water at the same temperature as the solution. The apparent molar volume of the solute in a pure aqueous solution is related to the total volume of the solution V (cm^3) by:

$$V^\phi = (V - n_w V_w^o)/n_s \qquad (2)$$

where V_w^o (cm^3 mol^{-1}) is the molar volume of pure water at the temperature of interest.

Apparent molar volumes of electrolytes at infinite dilution in water (i.e., at zero concentration) are additive in terms of the individual ions (e.g., Millero, 1971) so that, for example:

$$V^{\phi\infty}(CH_3NH_3Cl) = V^{\phi\infty}\left(CH_3NH_3^+\right) + V^{\phi\infty}(Cl^-) \qquad (3a)$$

and

$$V^{\phi\infty}(MMAS) = 2V^{\phi\infty}\left(CH_3NH_3^+\right) + V^{\phi\infty}\left(SO_4^{2-}\right) \qquad (3b)$$

where $V^{\phi\infty}$ is apparent molar volume of the solute or ion at infinite dilution in water. By convention $V^{\phi\infty}$ (H^+) is set equal to zero at all temperatures, thus allowing other individual ionic values to be determined from those of electrolytes.