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Hydrates in binary sulfuric acid-water vapor: Comparison of CIMS measurements with the liquid-drop model

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Abstract. We report calculations of the distribution of sulfuric acid-water hydrates under atmospheric conditions using the liquid-drop hydrate model. The model-computed total acid concentrations (free acid plus hydrated acid) are compared with chemical ionization mass spectrometer (CIMS) measurements of total sulfuric acid vapor over solutions of varying concentration [*Marti et al.*, 1997] Results from this first direct comparison with experimental measurement suggest that the liquid-drop model overestimates the extent of hydrate formation. We explore the consequences of this overestimation on binary sulfuric acid-water nucleation rates, and on higher-order multicomponent nucleation rates involving these and additional trace species in the atmosphere. In particular, it is found that overestimation of hydrate formation by the model can result in substantial underprediction of sulfuric acid-water nucleation rates.

Introduction

The formation of gas-phase hydrates of sulfuric acid has a major influence on the thermodynamics of sulfuric acid-water nucleation and on the kinetics of particle growth [*Jaecker-Voirol et al.*, 1987; *McGraw*, 1995]. Thermodynamics dominates nucleation, and calculated rates differ enormously depending on whether or not hydrates are taken into account. This strong dependence arises because the saturation properties of the vapor are determined by the ratio of actual to equilibrium vapor pressures of the pure component species, i.e., unassociated water vapor and unassociated (free) sulfuric acid. These ratios define the water vapor relative humidity (RH) and relative acidity (RA), respectively, on which the driving free energy for nucleation depends. For a given total sulfuric acid concentration in the vapor, the formation of hydrates lowers the relative acidity by tying up a substantial fraction of the free sulfuric acid. This results in a higher thermodynamic nucleation barrier, and therefore a more stabilized vapor and correspondingly lower nucleation rate, then would be the case in the absence of hydrate formation. Equivalently, the greater the extent of hydration, the more total sulfuric acid is required to maintain a specified RA. Particle growth kinetics, on the other hand, is controlled to a greater extent by collision kinetics between the particle and each of the various condensing species present in the vapor, free and hydrated [*Schelling and Reiss*, 1981; *Taleb et al.*, 1997]. Athough the dependence on hydration is stronger for nucleation than for particle growth, the hydrate distribution needs to be taken into account nevertheless to obtain an accurate representation of particle growth.

Recently a set of measurements has been made of the total vapor phase sulfuric acid concentration [*Marti et al.*, 1997] that is suitable for comparison with the predictions of hydrate models. The primary objective of this letter is to make this comparison. We examine gas-phase hydration of sulfuric acid within the context of the liquid-drop hydrate model. The liquid-drop model extends capillary concepts of bulk free energy and bulk surface tension to molecular hydrate clusters [*Jaecker-Voirol et al.*, 1987; *Kulmala et al.*, 1991]. Although this is a questionable procedure, in the absence of reliable molecular descriptions of clustering it is frequently used to predict and to correct for the effects of hydrates in calculations of binary and multicomponent nucleation rates and rates of particle growth. The present comparison should, therefore, provide a means of assessing the effect of hydration for such applications.

Measured and Predicted Acid Vapor Concentrations

Marti et al. (1997) determined sulfuric acid vapor pressures by measuring the evaporation rate from particles of known size (large enough that the effects of surface curvature on vapor pressure can be ignored) and composition. Gas phase measurements were made by chemical ionization mass spectroscopy (CIMS), which enabled detection of sulfuric acid vapor down to concentrations below 10^5 molecules/cm^3. It is important to note that the CIMS measurements are sensitive to total acid without discrimination between free acid and monoacid hydrates, or even between free- and higher-order acid clusters (sulfuric acid dimers, trimers, etc.) and their hydrates [*Eisele and Tanner*, 1993]. As shown below, clusters containing two or more acid molecules can also be evaluated using the liquid-drop model. However, these species make a negligible contribution to the vapor composition, and for this reason we consider here only the monoacid hydrate distribution. Hence the total acid concentration measured by CIMS is:

$$N_{aT} \cong N_a + \sum_{h=1}^{\infty} N_h \qquad (1)$$

where N_a is the concentration of free acid. The summation gives the total concentration of hydrate clusters (each containing a single acid molecule and h waters). Using Eq. 1, CIMS measurements for N_{aT} can be combined with estimates (described below) of N_a to obtain a prediction for the total concentration of hydrate clusters. (Note that because the concentration of water vapor greatly exceeds that of sulfuric

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acid, the effect of hydrate formation on the water vapor balance can be ignored.)

Figure 1 shows the measured total acid vapor pressure of Marti et al. (1997), the vapor pressure of free acid, and the present calculation (described below) of the total acid vapor pressure obtained by summation over the free acid and hydrated acid distribution for each of two solution models. Note that as the concentration of acid in solution is reduced, the CIMS measurements show increasingly higher pressures than are accounted for by the vapor pressure of free acid. In the following section we will show that these positive deviations of the measurements from the corresponding free acid predictions are consistent with hydrate formation.

Calculation of the Acid-Hydrate Distribution: The Liquid-drop hydrate model

The liquid-drop hydrate model was developed primarily to account for the presence of hydrates in determining the vapor phase activity of sulfuric acid for calculations of binary sulfuric acid-water nucleation rates [*Jaecker-Voirol et al.*, 1987; *Kulmala et al.*, 1991]. The number concentration of hth hydrate, defined as a vapor-phase cluster having 1 acid and $h \geq 1$ water molecules, $H_2SO_4(H_2O)_h$, is:

$$N_h = N_T \exp(-W_h / kT) \cong N_w \exp(-W_h / kT) \qquad (2a)$$

where

$$W_h = h(\mu_w - \phi_w) + (\mu_a - \phi_a) + \sigma(1,h)A(1,h) \qquad (2b)$$

is the reversible work of hydrate formation in the liquid-drop model. In Eq. 2a, N_T is the total number concentration of vapor phase species, which is dominated by free water molecules, N_w. In Eq. 2b, ϕ_w and ϕ_a are the chemical potentials of water and free acid in the vapor phase, and μ_w and μ_a are the chemical potentials of water and acid in a bulk solution having the composition of the hydrate. The surface tension $\sigma(1,h)$ is that of the hydrate, which is approximated as the bulk surface tension over the solution of hydrate composition. The surface area of the hydrate (assumed spherical), $A(1,h)$, is computed from the partial molecular volumes of each of the species present in this same bulk solution. Curvature corrections to the surface tension are neglected in the liquid-drop model.

To obtain the hydrate distribution, we first rewrite Eq. 2 using

$$\begin{aligned} \mu_w - \phi_w &= -kT \ln(N_w / N_w^{sol}) \\ f_w &\equiv -kT \ln(N_w^{sol} / N_w^{\infty}) = -kT \ln(x_w \gamma_w) \\ \mu_a - \phi_a &= -kT \ln(N_a / N_a^{sol}) \\ f_a &\equiv -kT \ln(N_a^{sol} / N_a^{\infty}) = -kT \ln(x_a \gamma_a) \end{aligned} \qquad (3)$$

where N_w^{sol} and N_a^{sol} are the equilibrium vapor concentrations of water and free acid over a bulk solution having the composition of the hydrate, and N_w^{∞} and N_a^{∞} are the corresponding equilibrium concentrations over pure liquid water and pure liquid sulfuric acid, respectively. The activity coefficients of water and acid in solution, γ_w and γ_a are obtained from the empirical solution models described below. The quantities f_w and f_a are the differences in chemical potential between a molecule in its pure liquid state, water and acid respectively, and in solution. Thus, from Eqs. 3

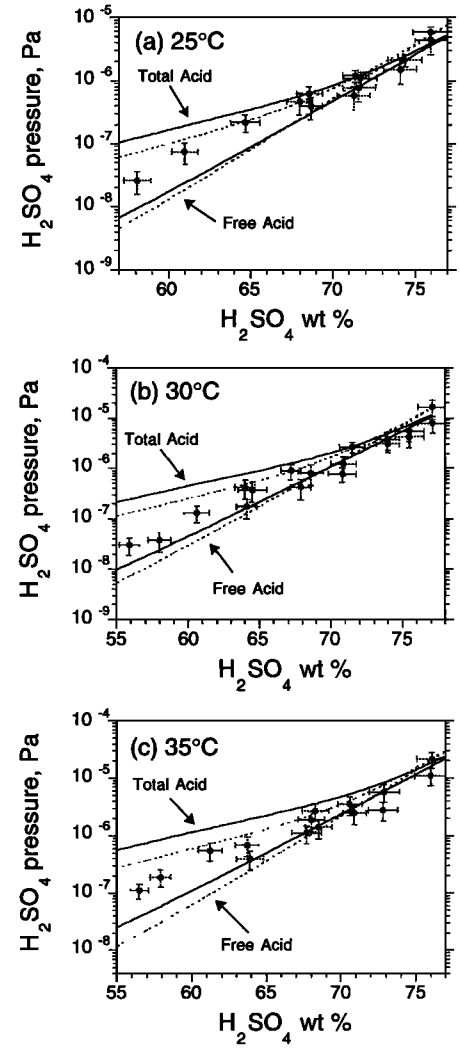

Figure 1. Sulfuric acid vapor pressure in pascals (1 Pa = 10 dyn/cm²) over sulfuric acid-water solutions of varying concentration. Data points are chemical ionization mass spectrometer (CIMS) measurements of Marti et al. (1997). The lower curves (solid and dashed) are the predicted partial vapor pressures of unhydrated sulfuric acid monomer. Upper curves (solid and dashed) are predicted total sulfuric acid vapor pressures (free acid monomer plus hydrates) from the liquid-drop hydrate model. Solid curves (upper and lower) were obtained using the thermodynamic model of Taleb et al. (1996) and sulfuric vapor pressure measurements of Ayers et al. (1980). Dashed curves (upper and lower) were obtained using the computer code AEROMIX, which is based on the thermodynamic model of Clegg et al. (1997).

$$\begin{aligned} Exp\left(-h\frac{\mu_w - \phi_w}{kT} - h\frac{f_w}{kT}\right) &= (S_w)^h \\ Exp\left(-\frac{\mu_a - \phi_a}{kT} - \frac{f_a}{kT}\right) &= S_a \end{aligned} \qquad (4)$$

where

$$\begin{aligned} S_w &\equiv N_w / N_w^{\infty} \\ S_a &\equiv N_a / N_a^{\infty} \end{aligned} \qquad (5)$$

are the relative humidity and (free acid) relative acidity, respectively. Equation 2a becomes:

$$N_h = N_w (S_w)^h S_a \mathrm{Exp}\left(h\frac{f_w}{kT} + \frac{f_a}{kT} - \frac{\Omega_h}{kT} \right) \quad (6)$$

for $h \geq 1$, where $\Omega_h \equiv \sigma(1,h)A(1,h)$ is the last term in Eq. 2b. Hydrates are thus seen as clusters in the vapor whose distribution is given by the Boltzmann factor in Eq. 2a, or more conveniently for our application, by Eq. 6.

For completeness we list equilibrium vapor pressures for the pure liquid components, sulfuric acid and water. Pressures are expressed in cgs units (dyn/cm^2) and temperatures in degrees K. For water [*Tabata*, 1973]:

$$P_w^\infty(T) = \mathrm{Exp}(26.3169 - 4207.24/T - 163963/T^2) \quad (7)$$

and for sulfuric acid [*Ayers et al.*, 1980]:

$$P_a^\infty(T) = \mathrm{Exp}(30.0877 - 10156/T). \quad (8)$$

Division of the pressure by kT gives the number concentrations appearing in the denominators of Eqs. 5.

In the absence of a bulk solution, with which the vapor can be in equilibrium (the usual situation under atmospheric conditions), Eqs 1, 6, and 8 can be used to estimate the free acid concentration ($N_a = P_a / kT$) and relative acidity (S_a) needed for predicting nucleation rates, provided the total acid vapor concentration, relative humidity, and temperature are known. In the experiments of Marti et al. (1997), a bulk solution was present and the free acid concentration and RH can be obtained from Eqs. 3, 8, and the activity coefficients of acid and water in the solution. This is the situation we now describe.

We first determine the relative humidity (S_w) and relative acidity (S_a) over bulk acid-water solutions of the appropriate temperature and composition for use in Eq. 6. These are readily obtained from Eq. 3, since for equilibrium with bulk solution $N_w = N_w^{sol}$ and $N_a = N_a^{sol}$. Additional calculations, requiring the use of thermodynamic solution models, are then carried out to obtain f_w and f_a from the corresponding activity coefficients, for the bulk solutions of Marti et al. (1997), and for solutions having the various hydrate compositions. The results shown in Figure 1 were obtained using two recently described solution models. Solid curves in the figure are based on the ternary solution (sulfuric acid-nitric acid-water) vapor pressure correlation of Taleb et al. (1996) applied to the sulfuric acid-water subsystem. Dashed curves are based on results obtained from the computer code AEROMIX, which performs calculations using the multicomponent solution model developed by Clegg and co-workers [see for example *Clegg et al.*, 1997]. Values of Ω_h are computed from temperature- and composition-dependent surface tension and volumetric data following Schelling and Reiss (1981). The lower curves in Figure 1 give the vapor pressure due to free acid $P_a = N_a kT = N_a^{sol} kT$. Note that the liquid-drop hydrate model is not used to obtain these lower curves. (The differences between these curves are apparently due to differences in the empirical data sets incorporated into the solution models.) The upper curves show the calculated total acid pressure $P_{aT} = N_{aT} kT$ obtained by summation over free acid and the hydrate distribution (Eq. 1) from the liquid-drop model. The mono- and di-hydrate species dominate the distribution at highest RH, which occurs over the more dilute acid solutions. The concentration of hydrates falls off sufficiently rapidly, with increasing number of water molecules h, that species for which h exceeds 6 make essentially no contribution. Thus $h = 6$ is used as a convenient break point for truncating the hydrate summation in Eq. 1.

Predictions of the total sulfuric acid vapor pressure from the liquid-drop hydrate model agree qualitatively with the CIMS measurements. As the acid weight percent in solution increases, the relative humidity above that solution is reduced. For example, at T= 30°C and 75 weight percent acid, the RH is approximately 3%. Under these conditions the vapor is dominated by free acid (i.e., the curves for the free acid and total acid begin to coincide), and the vapor pressure is in good agreement with the CIMS measurements. More dilute acid solutions are associated with higher relative humidity. For example, at T=30°C and 55 weight percent acid, the RH is approximately 28%, and most of the vapor-phase acid is in hydrated form. Under these conditions the liquid-drop model predicts a total acid vapor pressure that is about an order of magnitude higher than the free acid pressure, indicating that only about 10% of the acid molecules remain unhydrated. This trend is seen clearly in Figure 1 and is consistent with the CIMS measurements, which also show positive deviation from the free acid pressure, albeit not so great as that indicated by the model.

Though the liquid drop model and CIMS measurements agree qualitatively, Figure 1 shows that the liquid drop model over predicts the extent of hydrate formation. This deviation may point to limitations with the liquid drop model, although contributions due to a systematic experimental error cannot be ruled out. Because Marti et al. (1997) did not directly measure the equilibrium sulfuric acid vapor pressure, a systematic error which varied with hydration would produce a similar discrepancy. One possibility is that the CIMS detection efficiency for sulfuric acid decreased with increasing hydration due to lower sulfuric ionization efficiencies for hydrated acids. Tanner and Eisele (1995) experimentally studied the ionization efficiencies at various water vapor concentrations (sulfuric hydration) and found that, to within experimental uncertainty, the detection efficiency was independent of water concentration. Marti et al. (1997) explored other possible systematic errors, but found no significant bias in their measurements. Although other systematic errors may exist, given the assumptions inherent to the liquid drop model and uncertainty in the solution properties, it is very plausible that current models do not accurately predict the degree of sulfuric hydration.

Implications For Atmospheric Particle Formation

The classical binary nucleation rate, J, is proportional to the number of nuclei of critical size, which in the liquid-drop model is simply a generalization of Eqs. 2 and 6 to an arbitrary number of acid molecules in the cluster. Specifically, $J \propto (S_w)^{i*}(S_a)^{j*}$ where $i*$ and $j*$ are the numbers of water and acid molecules in the critical nucleus [*Jaecker-Voirol and Mirabel*, 1988]. To observe the effect that an overestimation of hydrate formation by the liquid drop model would have on nucleation rate, consider the vapor over a solution of approximately 61 acid weight percent at T=25°C, for which the RH is 0.2. Figure 1a shows about an order of magnitude difference between free acid pressure and the total acid pressure obtained from the liquid drop model (and about a half order of magnitude difference, depending on which solution model is used, between

the free acid pressure and measured total acid pressure) under these conditions. These factors are predicted to be independent of the actual values of N_a (*cf.* Eqs. 1, 5, and 6). In the absence of hydrates, classical binary nucleation theory predicts a nucleation rate of order $J = 1$ cm^{-3} s^{-1} under these conditions for RA = 0.005, corresponding to $N_a = 2.3 \times 10^9$ cm^{-3}. (If there were no hydrates, this would be the total acid concentration required for nucleation to occur.) According to the liquid drop model the total acid concentration required to achieve the same free acid RA, and therefore about the same nucleation rate, is actually an order of magnitude higher. Alternatively, for a fixed total acid measurement, any model overestimate of the degree of hydration translates to an underestimate of free acid RA, entering the classical expression for the nucleation rate, resulting in a much larger underestimate of the rate itself. Thus for j* = 10, a typical value under atmospheric conditions [*McGraw*, 1995], a half order of magnitude underestimate of S_a corresponds to a factor of 10^5 underestimate of J.

Field measurements [*Weber et al.*, 1997] suggest rates of nucleation that greatly exceed predictions based on binary sulfuric acid-water nucleation theory. The differences, however, are apparently too large to be accounted for by uncertainties in the hydrate distribution - even if all of the measured total acid molecules were free. Recent measurements suggest that additional trace species (perhaps ammonia) can act, via a ternary nucleation mechanism, to enhance the binary nucleation rate [*Weber et al.*, 1998]. The ternary nucleation rate follows as an extension of the binary case. Thus $J \propto (S_w)^{i*}(S_a)^{j*}(S_x)^{k*}$ where x is the third component and $k*$ is the number of molecules of x in the critical nucleus. Computation of the relative acidity, S_a, and its coupling to RH through hydrate formation, is unchanged from the binary case.

In this letter we have shown that the departure of CIMS vapor pressure measurements observed by Marti et al. (1997), from the free-acid predictions, are consistent with hydration of sulfuric acid in the vapor phase. The CIMS data suggest that the liquid drop hydrate model tends to overestimate the extent of hydrate formation and that more sophisticated models of hydration are required. For example, an *ab initio* study of gas-phase sulfuric acid hydrates containing 1 to 3 water molecules has recently been completed [*Arstila et al.*, 1998]. These results, although limited to calculation of hydration enthalpy, rather than free-energy, are indicative of less hydration than expected from the capillary drop model, in direction with the experimental comparison of Figure 1. In a very recent study, Kusaka et al. (1998) used Monte Carlo simulations based on a parameterized *ab initio* potential to obtain the hydrate distribution. For their adopted *ab initio* potential these authors found extensive hydration -- the probability that an acid molecule is unhydrated at 298K is smaller by 3-4 orders of magnitude (depending on RH) than the capillary drop model prediction. This trend is in opposite direction from the experiments profiled in Figure 1 and would suggest that the drop model underestimates hydration. Kusaka et al. point out, however, that the hydrate fraction is highly sensitive to the intermolecular potential parameterization used in the model. Using a different set of *ab initio* results, the acid molecules showed no significant hydration [*Kusaka et al.*, 1998]. In the present letter we have shown that it is now feasible to compare hydrate models with experiment. Measurements over more dilute acid solutions would be especially valuable for guiding the development of improved hydrate models for geophysical applications. These applications include the conversion from total acid to free acid that will be required in models representing formation of atmospheric aerosols from oxidation of SO_2. In a future study we will present a parameterization of the hydrate distribution suitable for use in such models.

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References

Arstila H., K. Laasonen, and A. Laaksonen, Ab initio study of the gas-phase sulphuric acid hydrates containing 1 to 3 water molecules, *J. Chem. Phys. 108*, 1031-1039, 1998.

Ayers G. P., R. W. Gillett, and J. L. Gras, On the vapor pressure of sulfuric acid, *Geophys. Res. Lett. 7*, 433-436, 1980.

Clegg S. L., P. Brimblecombe, and A. S. Wexler, A thermodynamic model of the system H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures, *J. Phys. Chem. A 102*, 2137-2154, 1998.

Eisele F. L. and D. J. Tanner, Measurements of the gas phase concentrations of H_2SO_4 and methane sulfonic acid and estimates of H_2SO_4 production and loss in the atmosphere, *J. Geophys. Res. 98*, 9001-9010, 1993.

Jaecker-Voirol A., P. Mirabel, and H. Reiss, Hydrates in supersaturated binary sulfuric acid-water vapor: A reexamination, *J. Chem. Phys. 87*, 4849-4852, 1987.

Jaecker-Voirol A. and P. Mirabel, Nucleation rate in a binary mixture of sulfuric acid and water vapor, *J. Phys. Chem. 92*, 3518-3521, 1988.

Kulmala M., M. Lazaridis, A. Laaksonen, and T. Vesala, Extended hydrates interaction model: Hydrate formation and the energetics of binary homogeneous nucleation, *J. Chem. Phys. 94*, 7411-7413, 1991.

Kusaka I., Z.-G. Wang, and J. H. Seinfeld, Binary nucleation of sulfuric acid-water: Monte Carlo simulation, *J. Chem. Phys. 108*, 6829-6847, 1998.

Marti J. J., A. Jefferson, X. P. Cai, C. Richert, P. H. McMurry, and F. Eisele, H_2SO_4 vapor pressure of sulfuric acid and ammonium sulfate solutions, *J. Geophys. Res. 102*, 3725-3735, 1997.

McGraw R., Two-dimensional kinetics of binary nucleation in sulfuric acid-water mixtures, *J. Chem. Phys.102*, 2098-2108, 1995.

Schelling F. J., and H. Reiss, Time lag in nucleation: A variational treatment of relaxation times in the binary sulfuric acid-water system, *J. Chem. Phys. 74*, 3527-3531, 1981)

Tabata S., A simple but accurate formula for the saturation vapor pressure over liquid water, *J. Appl. Meteorol. 12*, 1410-1412, 1973.

Taleb D.-E., J-L Ponche, and P. Mirabel, Vapor pressures in the ternary system water-nitric acid-sulfuric acid at low temperature: A reexamination, *J. Geophys. Res., 101*, 25967-25977, 1996.

Taleb D.-E., R. McGraw, and P. Mirabel, Time lag effects on the binary homogeneous nucleation of aerosols in the wake of an aircraft, *J. Geophys. Res., 102*, 12885-12890, 1997.

Tanner D. J., and F. L. Eisele, Present OH measurement limits and associated uncertainties, *J. Geophys. Res., 100*, 2883-3892, 1995.

Weber R. J., J. J. Marti, P. H. McMurry, F. L. Eisele, D. J. Tanner, and A. Jefferson, Measurements of new particle formation and ultrafine particle growth rates at a clean continental site, *J. Geophys. Res. 102*, 4375-4385, 1997.

Weber, R. J., P. H. McMurry, L. Mauldin, D. Tanner, F. Eisele, F. Brechtel, S. Kreidenweis, G. Kok, R. Schillawski, D. Baumgardner, A study of new particle formation and growth involving biogenic trace gas species measured during ACE-1, *J. Geophys. Res.*, in press, 1998.

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