Solubility of Methanol in Low-Temperature Aqueous Sulfuric Acid and Implications for Atmospheric Particle Composition

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Using traditional Knudsen cell techniques, we find well-behaved Henry's law uptake of methanol in aqueous 45−70 wt % H_2SO_4 solutions at temperatures between 197 and 231 K. Solubility of methanol increases with decreasing temperature and increasing acidity, with an effective Henry's law coefficient ranging from 10^5 to 10^8 M atm^{-1}. Equilibrium uptake of methanol into sulfuric acid aerosol particles in the upper troposphere and lower stratosphere will not appreciably alter gas-phase concentrations of methanol. The observed room-temperature reaction between methanol and sulfuric acid is too slow to provide a sink for gaseous methanol at the temperatures of the upper troposphere and lower stratosphere. It is also too slow to produce sufficient quantities of soluble reaction products to explain the large amount of unidentified organic material seen in particles of the upper troposphere.

Introduction

High levels of methanol (400−800 ppt) have been observed in the middle and upper troposphere over the Atlantic and Pacific oceans.[1,2] The only available estimate of the global methanol (CH_3OH) budget implies that a significant unknown sink of this oxygenated species must exist in the atmosphere.[1] Possible interactions between methanol and sulfate aerosols are examined here to evaluate the roles of solubility and reactivity as sinks of gaseous methanol in the upper troposphere (UT) and lower stratosphere (LS).

Organic compounds have been detected in most particles studied in the UT/LS with the PALMS laser mass spectrometrometer.[3,4] Identification and quantitation of this organic material is difficult with present techniques, but Murphy et al.[3] report that aerosols sampled in the UT often contained more organic material than sulfate. Filter samples collected during the INDOEX mission gave similar results. Novakov et al.[5] report that the organic carbon loading was approximately half that of sulfate under polluted conditions in the tropical Indian Ocean region. Resolving the source and composition of this organic material is important for understanding the physical, optical, and chemical properties of atmospheric aerosols. At UT/LS altitudes, possible gaseous precursors for this condensed organic material include methanol, acetone, and formaldehyde.

Several laboratory studies[6−9] have shown that acetone is not sufficiently soluble ($H^* = 10^4{-}10^6$ M atm^{-1}) or reactive in aqueous sulfuric acid (H_2SO_4) under normal UT/LS conditions to account for the high levels of condensed-phase organics inferred from field measurements and laboratory calibrations.[3,5,10] Similarly, the solubility of formaldehyde ($H^* = 10^5{-}10^7$ M atm^{-1})[11,12] is too low for equilibrium uptake to account for the field observations. However, polymerization and prolonged uptake of formaldehyde in aqueous H_2SO_4 may form long-chain organic species in acidic particles.[11]

Here we present measurements of methanol solubility in low-temperature aqueous sulfuric acid solutions. Further, we evaluate whether methanol solubility or reactivity in aqueous H_2SO_4 can partially explain the imbalanced global methanol budget and/or the presence of ubiquitous organic material in atmospheric sulfate aerosols.

Experimental Techniques

The solubility of methanol in aqueous sulfuric acid solutions was measured using the Knudsen cell technique, which has been described in detail elsewhere.[9,13−15] The apparatus consists of two Teflon-coated Pyrex chambers separated by a valve, the lower of which contains ∼6 mL of sulfuric acid solution. The lower chamber is suspended in a cold bath, and several thermocouples are mounted on the outside of the cell wall to measure the temperature. When the two thermocouples nearest the surface of the acid sample were not in agreement, they were averaged, leading to a temperature uncertainty on the order of ±1 K.

Gaseous methanol is admitted to the upper chamber through a capillary and exits through a calibrated aperture to a differentially pumped mass spectrometer (Balzers QMG 421C electron ionization quadrupole system). The total pressure in the cell is generally kept below ∼20 mTorr to maintain molecular flow conditions. A stable flow of methanol is established, and water vapor is introduced to match the vapor pressure of water over the sulfuric acid solution to prevent changes in the acid composition. To begin an experiment, the valve separating the two chambers is opened, and methanol is exposed to the sulfuric acid. The uptake of methanol by the solution is observed as a decrease in the mass spectrometer signal, monitored at $m/z = 31$ (CH_3O^+).

The uptake coefficient (γ) is defined as the fraction of incident molecules which are taken up by the surface. The number of molecules lost to the surface is measured by the change in flow, $F_o - F$, out of the cell upon exposure, where F_o is the flow

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before exposure (molecules s^{-1}) and F is the flow during exposure.

$$\gamma = \frac{A_h}{A_s}\left(\frac{F_o - F}{F}\right) \tag{1}$$

Because the mass spectrometer signal is proportional to the flow of molecules out of the cell, the signal can be used directly in the calculation, where A_h is the area of the escape aperture (either 0.018 or 0.049 cm^2) and A_s is the surface area of the H_2SO_4 sample (5.7 cm^2).

As the exposed portion of the acid solution becomes more concentrated in methanol, the net uptake decreases, and thus time-dependent measurements of γ allow for determination of the solubility. The rate of methanol diffusion into the bulk liquid, coupled with the overall solubility and any reaction which occurs, controls the time dependence of γ according to the equation (e.g., Kolb et al.,[16] Finlayson-Pitts and Pitts[15]):

$$\frac{1}{\gamma} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{\sqrt{\pi}\bar{c}}{4RTH^*\sqrt{D}}\left(\frac{1}{t^{-1/2} + \sqrt{\pi k}}\right) \tag{2}$$

where time, t, is given in seconds, $\bar{c}$ is the average molecular velocity ($(8k_BT/\pi m)^{1/2}$), R is the gas constant, T is absolute temperature, D is the diffusion coefficient in the condensed phase, α is the mass accommodation coefficient, k is the pseudo-first-order rate coefficient, and Γ_g characterizes any limitation due to gas-phase diffusion. A plot of $1/\gamma$ versus $(t^{-1/2} + \sqrt{\pi k})^{-1}$ should be linear with a slope that yields $H^*\sqrt{D}$, from which the effective Henry's law coefficient H^* (M atm^{-1}) can be extracted if the diffusion coefficient is known. (The Henry's law coefficient, H, is defined for physical solvation only, but in many systems additional processes lead to increased solubility. Deno and Wisotsky[17] report that methanol is 61% protonated in a 45 wt % H_2SO_4 solution, indicating that this channel contributes significantly in all solutions studied here. Thus we report the effective Henry's law coefficient, which includes uptake due to physical solvation as well as any rapid equilibration which may occur in solution.)

Diffusion coefficients were calculated by the technique of Klassen et al.:[18] $D = cT/\eta$, where c (cm^2 cP s^{-1} K^{-1}) is a constant that depends on the solvent and the diffusing species, and η (cP) is the viscosity of the liquid. For methanol in sulfuric acid, c was estimated at 6.8×10^{-8} using a value of 37 cm^3 mol^{-1} for the molar volume of methanol (Le Bas additivity rules, Reid et al.[19]) and the empirical relation of Wilke and Chang.[20] Viscosities were calculated from Williams and Long.[21]

The rate coefficient, k, for methanol reaction with H_2SO_4 has been measured at room temperature[22,23] and can be estimated to be on the order of 10^{-10} s^{-1} for our experimental conditions. Values as small as this exerted no discernible influence on the values of H^* obtained, thus the results reported here were obtained by setting $k = 0$. See the Appendix for a discussion of the literature values and their extrapolation to low temperatures, and see the section regarding reaction between methanol and H_2SO_4 for a discussion of the sensitivity of H^* to k.

Sulfuric acid solutions were prepared from 95.8% sulfuric acid (Mallinckrodt) and deionized water (Millipore). The solutions were titrated and found to have concentrations of 45.3 ± 0.4, 60.7 ± 0.5, and 72.2 ± 0.3 wt % H_2SO_4. A magnetic stir bar in the sulfuric acid solution allowed the sample to be stirred (≥ 10 min) between experiments. Gas-phase methanol (Mallinckrodt) and water were taken from the vapor above liquid samples which were purified with at least one freeze−pump cycle each day. The water vapor flow rate was adjusted to give a partial pressure in the Knudsen cell which matched the vapor pressure of the sulfuric acid solution. Methanol partial pressures used were in the range of $\sim 1 \times 10^{-5}$ to 2×10^{-4} Torr.

As an independent method of measuring H^*, we also performed measurements of the equilibrium vapor pressure of methanol over $CH_3OH/H_2SO_4/H_2O$ solutions of known concentrations. The mass spectrometer response for methanol was calibrated each day using the vapor over a sample bulb of methanol and a Baratron capacitance manometer attached to the cell. In this way, the signal recorded by the mass spectrometer during an experiment could be directly converted to an absolute methanol partial pressure, thus allowing direct measurement of the vapor pressure over the known ternary solutions. Methanol/acid solutions were prepared at room temperature by adding a known volume of methanol to the same sulfuric acid solutions used for the uptake measurements described above, such that methanol concentrations were 0.20 M in each case. Immediately after mixing, a sample was loaded into the bottom of the cell and cooled to ∼230 K. Samples were cooled within 20 min of mixing, and all cold temperature measurements were made within 10 h.

The cell was evacuated, and appropriate flows of both water and methanol vapor were supplied to prevent the surface layer from changing composition due to desorption. The use of the small escape aperture and the addition of $CH_3OH(g)$ prevented condensed-phase diffusion limitations, ensuring that the steady-state partial pressure observed was equivalent to the equilibrium vapor pressure, rather than an intermediate pressure established due to competition between desorption and pumping. The solution was stirred throughout the experiment to keep the surface composition the same as that of the bulk. The valve separating the solution from the mass spectrometer was opened and the partial pressure was recorded. To confirm that the steady state partial pressure observed over the solution was truly the equilibrium vapor pressure, the measurement cycle was repeated several times with slightly different flow rates of methanol. Partial pressures slightly larger and smaller than the equilibrium vapor pressure were tested to ensure that net uptake and desorption occurred as expected. The effective Henry's law coefficient was then calculated from the relation $H^* = C/P$, where C is the solution concentration of methanol and P is the experimentally determined methanol vapor pressure over the solution. This process was then repeated at several different temperatures.

Results

A representative uptake measurement is shown in Figure 1. Panel (a) shows the mass spectrometer data as a function of time when methanol ($\sim 1 \times 10^{-4}$ Torr) was exposed to 45 wt % H_2SO_4 at 221.7 K. The uptake is seen to decrease with time, as expected for a system where uptake due to solubility dominates over reaction. Panel (b) shows the inverse of the calculated uptake coefficient plotted against the square root of exposure time. From eq 2 with $k = 0$, the slope of this line yields the quantity $H^*\sqrt{D}$. Using the method of Klassen et al.[18] to determine the diffusion coefficient D, the value of H^* can be extracted. For the experiment shown here, $H^* = 1.4 \times 10^5$ M atm^{-1}.

Table 1 summarizes the exposure data collected for methanol dissolution into 45.3, 60.7, and 72.2 wt % H_2SO_4 solutions. These values of H^* are plotted as the open symbols in Figure 2. Uncertainty in the value of H^* comes from uncertainty in D (dominated by the ±20% uncertainty in viscosity[21]) and in determination of the slope through the data in the format shown

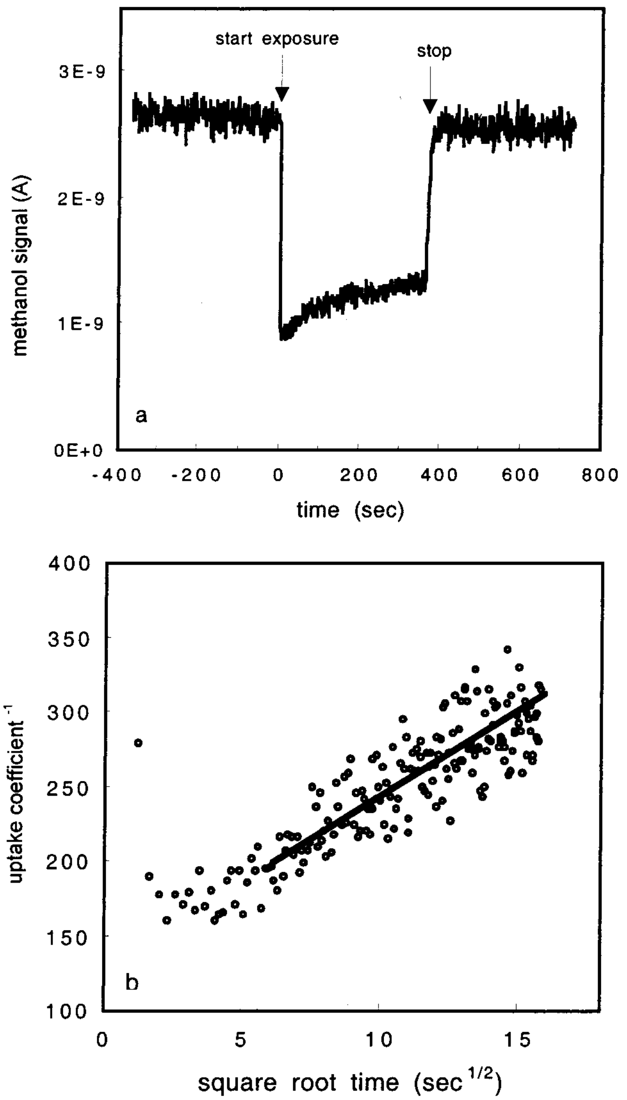

Figure 1. (a) Mass spectrometer signal ($m/z = 31$) for methanol before, during, and after exposure to 45 wt % H_2SO_4 at 221.7 K. Exposure was begun at $t = 0$ s. (b) Inverse of the uptake coefficient for the experiment in part (a), plotted against the square root of exposure time. The slope of this line gives $H^*D^{1/2}$, according to eq 2.

in Figure 1b. The latter is usually ≤20%, but for experiments with sparse or especially scattered $1/\gamma$ data, the slope could be as uncertain as a factor of 2.

Our data shows well-behaved Henry's law uptake of methanol in 45−70 wt % H_2SO_4 in the range of 197−223 K. Solubility increases with decreasing temperature and with increasing acidity, with values ranging from 10^5−10^8 M atm^{-1}. The increase in solubility with increasing acidity is consistent with protonation of methanol by a strong acid.

We have confirmed these data using the independent equilibrium technique described in the Experimental Techniques section. From measurements of the vapor pressure over known ternary $CH_3OH/H_2SO_4/H_2O$ solutions, the Henry's law coefficient can be determined without requiring knowledge of the diffusion coefficient. These data are reported in Table 2 and are shown in Figure 2 as the solid points. We see no difference between these two types of measurements, validating the estimates of D and indicating that no significant loss of methanol occurs at room temperature in the 10−20 min required to load and cool the sample. Also included in Figure 2 is an extrapolation of the values for methanol dissolution in water measured by Snider and Dawson[24] at 273 and 298 K.

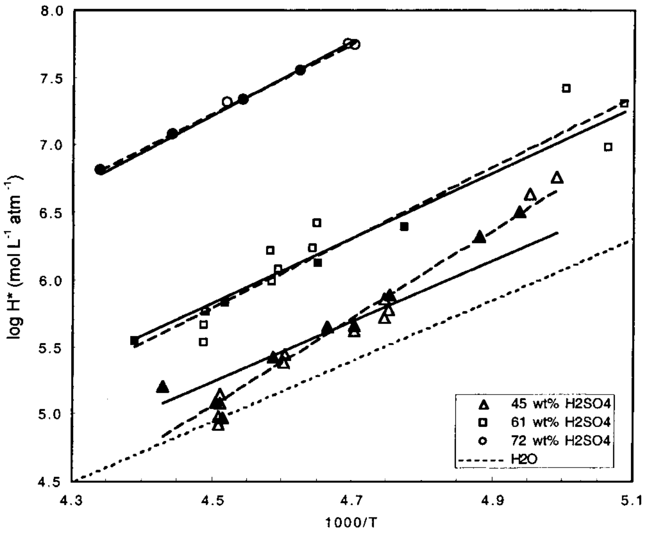

Figure 2. Effective Henry's law coefficient as a function of inverse temperature and acid composition. Data obtained using the uptake technique are plotted as open symbols; equilibrium measurements are shown as solid symbols. The dotted line is the solubility of methanol in water. Dashed lines are best-fits to the data, and the solid lines are fits with a fixed $\Delta S = -134$ J mol^{-1} K^{-1}.

TABLE 1: Experimental Conditions and Measured Effective Henry's Law Coefficients for Uptake of Methanol into H_2SO_4

H_2SO_4	T (K)	$H^*\sqrt{D}$	D (cm^2 s^{-1})	H^* (mol L^{-1} atm^{-1})
45.3 wt %	200.4	941	2.6×10^{-8}	5.9×10^6
	201.9	799	3.4×10^{-8}	4.3×10^6
	210.5	184	9.2×10^{-8}	6.1×10^5
	210.7	161	9.2×10^{-8}	5.3×10^5
	210.7	222	9.2×10^{-8}	7.3×10^5
	212.7	155	1.1×10^{-7}	4.6×10^5
	212.7	141	1.1×10^{-7}	4.2×10^5
	217.2	115	1.7×10^{-7}	2.8×10^5
	217.3	104	1.8×10^{-7}	2.4×10^5
	221.5	48	2.5×10^{-7}	9.5×10^4
	221.7	70	2.5×10^{-7}	1.4×10^5
	221.7	61	2.5×10^{-7}	1.2×10^5
	221.8	49	2.6×10^{-7}	9.6×10^4
	221.8	43	2.6×10^{-7}	8.4×10^4
60.7 wt %	196.6	1142	3.1×10^{-9}	2.0×10^7
	197.5	592	3.7×10^{-9}	9.7×10^6
	199.9	2014	5.9×10^{-9}	2.6×10^7
	215.1	579	4.7×10^{-8}	2.7×10^6
	215.4	385	4.9×10^{-8}	1.7×10^6
	217.7	294	6.1×10^{-8}	1.2×10^6
	218.1	247	6.4×10^{-8}	9.7×10^5
	218.2	413	6.4×10^{-8}	1.6×10^6
	222.7	180	9.9×10^{-8}	5.7×10^5
	222.8	111	1.0×10^{-7}	3.4×10^5
	222.8	148	1.0×10^{-7}	4.6×10^5
72.2 wt %	212.7	3474	4.0×10^{-9}	5.5×10^7
	213.1	3714	4.4×10^{-9}	5.6×10^7
	221.2	2566	1.5×10^{-8}	2.1×10^7

Combining the two types of measurements and doing a least-squares fit (dashed lines in Figure 2) allows a determination of the enthalpy and entropy of dissolution.[9]

$$\log H^* = A + 1000B/T \tag{3}$$

$$A = \Delta S°/2.303R + \log M_{\text{solv}} \tag{4}$$

$$B = -\Delta H°/2.303R \tag{5}$$

where M_{solv} is the molarity of water in the solution (mol L^{-1}).

TABLE 2: Experimental Conditions, Observed Methanol Vapor Pressures, and Effective Henry's Law Coefficients for Equilibrium Measurements

H_2SO_4	$[CH_3OH]$ (mol L^{-1})	T (K)	vapor pressure (atm)	H^* (mol L^{-1} atm^{-1})
45.3 wt %	0.20	202.6	6.2×10^{-8}	3.2×10^{6}
		205.0	9.5×10^{-8}	2.1×10^{6}
		210.4	2.6×10^{-7}	7.8×10^{5}
		214.5	4.4×10^{-7}	4.6×10^{5}
		218.1	7.5×10^{-7}	2.7×10^{5}
		222.0	1.6×10^{-6}	1.2×10^{5}
		225.8	1.2×10^{-6}	1.6×10^{5}
60.7 wt %	0.20	209.5	8.1×10^{-8}	2.5×10^{6}
		215.1	1.5×10^{-7}	1.3×10^{6}
		221.4	2.9×10^{-7}	6.8×10^{5}
		227.9	5.7×10^{-7}	3.5×10^{5}
72.2 wt %	0.20	216.3	5.5×10^{-9}	3.6×10^{7}
		220.2	9.2×10^{-9}	2.2×10^{7}
		225.2	1.7×10^{-8}	1.2×10^{7}
		230.5	3.1×10^{-8}	6.5×10^{6}

TABLE 3: Thermodynamic Parameters for Methanol in Aqueous Sulfuric Acid

	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	M_{solv} (mol L^{-1})	B	A	m (mol kg^{-1})
water	−43.4	−134	55.6	2.27	−5.26	
45 wt %	−62.7	−216	43.1			
61 wt %	−50.1	−144	34.2			
72 wt %	−49.8	−113	26.7			
45 wt %	−45.1	−134	43.1	2.35	−5.37	8.45
61 wt %	−48.0	−134	34.2	2.51	−5.47	15.76
72 wt %	−54.5	−134	26.7	2.85	−5.58	26.50

As shown in the upper portion of Table 3, we find $\Delta H = -62.7$, −50.1, and −49.8 kJ mol^{-1} and $\Delta S = -216$, −144, and −113 J mol^{-1} K^{-1} for 45.3, 60.7, and 72.2 wt %, respectively. While the fits to our data are quite good ($r^2 =$ 0.96, 0.93, and 1.0), a significant difference exists between the observed entropy values and the value of −134 J mol^{-1} K^{-1} for methanol uptake into water.[24] Even though protonation of the solute occurs[17,25] and some additional ordering of the solvent with increasing acidity should result in a more negative value for ΔS, we do not expect large changes in the entropy of solvation. For this reason, and because our fits actually give the largest difference (relative to water) for our most dilute acid solution, we have also fit the data by fixing $\Delta S = -134$ J mol^{-1} K^{-1} (solid lines in Figure 2). This yields enthalpies of −45.1, −48.0, and −54.5 kJ mol^{-1} for methanol uptake into 45.3, 60.7, and 72.2 wt % H_2SO_4 solutions (bottom portion of Table 3). The increasingly negative values of ΔH in more concentrated acid are due to an increasing degree of protonation. The magnitude of the change seen here is similar to that reported for acetone in aqueous H_2SO_4 solutions.[9]

The fits for the 72 and 61 wt % solutions are well within the error limits, but the fit for 45 wt % shows a larger deviation from the data. This is most evident at the ends of the temperature range studied, where we have fewer measurements. Because the set of enthalpies determined with the fixed entropy is based on a physical understanding of the solvation processes, we recommend using it and $\Delta S = -134$ J mol^{-1} K^{-1} for reasonable extrapolation outside the experimental temperature range. The best-fit parameters given in the top of Table 3 may be reasonable for interpolation within the range of temperatures studied here, but we have no physical explanation for why the entropy of dissolution into 45 wt % H_2SO_4 (−216 J mol^{-1} K^{-1}) would be distinctly different from that of dissolution into both water and 61 wt % H_2SO_4, which show values fairly similar to each other (−134 and −144 J mol^{-1} K^{-1}, respectively). The molality of H_2SO_4 varies from 8 to 26 mol kg^{-1} over the range 45−72 wt %, and any acid-dependent enhancement of solubility should be present for all solutions reported here. Thus, we believe the parameters derived with a fixed entropy are the best representation of the data. Within the estimates of our uncertainty, this third-law approach does not disagree with the data, and we believe it is a more correct interpretation of a small data set with obvious scatter.

Table 3 gives the coefficients needed to determine the effective Henry's law coefficients for the uptake of methanol into 45, 61, or 72 wt % H_2SO_4 solution at UT/LS temperatures. The molarity of water in the solution, M_{solv}, was calculated with a solution density estimated at 215 K.[26] To calculate methanol solubility in H_2SO_4 solutions other than those studied here, the value of A can be calculated according to eq 4, and B can be found from the following relation:

$$B = (6.19 \times 10^{-4})m^2 + (5.44 \times 10^{-3})m + 2.267 \qquad (6)$$

where m is the molality of the H_2SO_4 solution (moles H_2SO_4 per kg H_2O). Although the quadratic functional form has no explicit physical rationale, it fits the limited data extremely well, including the value of $B = 2.27$ for water from the data of Snider and Dawson.[24]

Slow Reaction between Methanol and H_2SO_4

It has long been known that primary alcohols will react with concentrated H_2SO_4 to form mono- and dialkyl sulfates,[22,27−29] so it is necessary to consider reaction as a parallel uptake process which may influence our solubility measurements at low temperatures. Few quantitative reports exist for methanol−sulfate "esterification," but the available data[22,23] are summarized in the Appendix. In this section we show that our data suggest $k \le 3 \times 10^{-5}$ s^{-1}.

Uptake Experiments. From inspection of the last term in eq 2, it can be seen that reaction will compete (~10%) with uptake due to solubility when $\sqrt{\pi k} \ge 0.1(t^{-1/2})$. For the uptake experiments presented here, $t^{-1/2} \ge 0.03$ (t generally ≤ 1225 s), so we can examine the time dependence of our data for evidence of reaction where $k > \sim 3 \times 10^{-6}$ s^{-1}. Figure 3 shows the data from an uptake of methanol on 72 wt % H_2SO_4 at 213 K plotted against $(t^{-1/2} + \sqrt{\pi k})^{-1}$ with different assumed values for k. When $k = 0$, this format is identical to that in Figure 1b.

Previous studies suggest $k \sim 10^{-10}$ s^{-1} under our low-temperature conditions (see Appendix), and the lower data set shows the observed $1/\gamma$ values plotted against $(t^{-1/2} + \sqrt{\pi k})^{-1}$ when $k = 1 \times 10^{-10}$ s^{-1}. As expected, the slope of a linear least-squares fit through the data (solid line) is indistinguishable to three significant digits from that obtained when $k = 0$ (not shown). The initial 36 s of data are omitted, as they may deviate from the theoretical line due to volume expansion in the cell.[30]

If we assume no temperature dependence to the reaction between methanol and sulfuric acid, we can obtain a more conservative test of the Henry's law coefficient obtained. A new set of x-values can be calculated by setting $k = 3 \times 10^{-4}$ s^{-1}, the room-temperature value observed by Vinnik et al.[23] The observed values of $1/\gamma$ are plotted against these x-values in the top data set of Figure 3 (top and right axes). This assumed value for k has begun to degrade the linearity of the original data set, and further increasing k only magnifies the disparity between the data and the theoretical linear dependence. The threshold for linearity is approximately $k \le 3 \times 10^{-5}$ s^{-1} (not shown); at

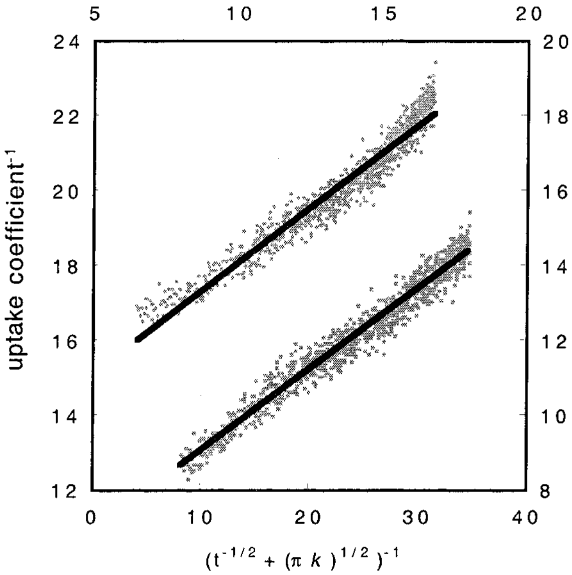

Figure 3. Inverse of the uptake coefficient for methanol on 72 wt % H_2SO_4 at 213 K plotted against $(t^{-1/2} + \sqrt{\pi k})^{-1}$ with different assumed values for *k*. The lower data set (bottom and left axes) assumes $k = 1 \times 10^{-10}$ s^{-1}, while the upper data set (top and right axes) uses $k = 3 \times 10^{-4}$ s^{-1}. The solid lines are linear fits to the data and are meant to highlight the curvature of the upper data set. See text for discussion.

larger assumed values of *k*, deviation of the data from the expected linear form becomes apparent.

Three possible explanations for the observed curvature when the data is plotted against $(t^{-1/2} + \sqrt{\pi k})^{-1}$ for $k > 3 \times 10^{-5}$ s^{-1} are the following: (a) eq 2 is not the correct theoretical form for the present data, (b) the data are incorrect, or (c) the rate coefficient for reaction between methanol and sulfuric acid is less than 3×10^{-5} s^{-1}. The treatment described by eq 2 is commonly employed, and because we can achieve linearity with $k < 3 \times 10^{-5}$ s^{-1}, we discount the first possibility. As to the second explanation, the Knudsen cell technique and this apparatus in particular have been shown to produce reasonable results for both solubility and reactivity measurements,[9,30,31] and thus we have no reason to suspect the data to be entirely at fault. Therefore, we believe that examining the data in this manner indicates that the rate coefficient for reaction of methanol with aqueous sulfuric acid at these temperatures is < 3×10^{-5} s$^{-1.}$

We have tried to fit our data to eq 2 to solve for *H**, *k*, and an intercept, but multiple solutions are possible within the scatter of the data. For example, the data shown in Figure 3 can be fit nearly indistinguishably with any of the following sets of values: 5.5×10^7, 0, and 0.093; 5.4×10^7, 1×10^{-7}, and 0.093; 5.4×10^7, 4.5×10^{-7}, and 0.092; 5.2×10^7, 1.1×10^{-6}, and 0.093; among others.

The large uncertainty in *k* indicates that its value cannot be determined well using this approach. Conversely, the value determined for *H** will not be significantly different for values of $k \leq 3 \times 10^{-5}$ s^{-1}. When $k = 3 \times 10^{-5}$ s^{-1}, the determined effective Henry's law coefficient is approximately 30% less than the value determined with $k = 0$. Therefore, within the bounds of *k* we can establish from our data, the value of *H** extracted from the observations varies by only 30%. Such a reduction in *H** implies only a 2 kJ mol^{-1} (0.5 kcal mol^{-1}) reduction in the free energy of solvation. Recall that the value of *k* expected at these temperatures is actually much lower ($\sim 10^{-10}$ s^{-1}) than our upper bound (see Appendix), suggesting that the true value of *H** is indistinguishable from that determined with $k = 0$ (see discussion of Figure 3 above).

It is desirable to extract the mass accommodation coefficient, α, from the intercept ($= 1/\Gamma_g + 1/\alpha$) of the fit to the data plotted as in Figure 1b. If the "resistance" due to gaseous diffusion is taken to be negligible in the molecular flow regime, we find α for methanol uptake into aqueous H_2SO_4 to be <0.1. In fact, the majority of our calculated α values fall at or below 0.025, but we cannot explain the observed variation, thus we hesitate to ascribe too much physical meaning to the intercept values.

Equilibrium Experiments. Although our data suffers no complications from reaction at low temperatures, it is expected that the reaction has a temperature dependence[32] which may lead to interference at room temperature. In contrast to the uptake measurements which were performed entirely at low temperature, our equilibrium experiments did involve a short period of time at room temperature after the methanol was mixed into the H_2SO_4. During the 10−20 min required to mix the solution, load the cell, and quench to cold temperatures, less than 5% of the initial methanol could have been converted using $k = 4.5 \times 10^{-5}$ s^{-1} from Deno and Newman[22] for 70 wt % H_2SO_4 at 298 K. Our estimated threshold for detection of methanol loss is ∼10−15% in these absolute measurements, so no influence of reaction will be detected with this technique.

To further confirm the slow rate of reaction between methanol and H_2SO_4, a 0.20 M solution of methanol in 72.2 wt % H_2SO_4 was allowed to react at room temperature for prolonged periods of time before cooling and measuring the vapor pressure. After the solution was mixed, one sample was cooled, and the vapor pressure was measured at 222 K. The remainder of the solution was then allowed to react at room temperature for several days, and the vapor pressure was measured at low temperature at several intervals. As a comparison, the same experiment was performed with a similar solution of acetone in aqueous sulfuric acid. No loss of acetone was detected over 5 days, consistent with the observation of Klassen et al.[9] that $K_{eq} \sim 10^{-6}$ M^{-1} for the dimerization of acetone to form mesityl oxide. In contrast, after 140 h the methanol vapor pressure (and thus its solution concentration) had decreased to approximately half its original value, as expected under the experimental conditions based on the value of $K_{eq} = [CH_3OSO_3H][H_2O]/[CH_3OH][H_2SO_4] = 2.3$ given by Deno and Newman.[22] This experiment confirms that reaction does happen at room temperature, even though it is too slow to interfere with our measurements.

Atmospheric Implications

In the atmosphere, the ratio of methanol found in the condensed phase to that remaining in the gas phase can be calculated from $R_{aq/g} = H^*LRT$, where *L* is the volume of condensed material (aerosol or cloud droplets) per volume of air.[33,34] Given the small volume of sulfate aerosol particles present in the upper troposphere and lower stratosphere ($L \sim 10^{-13}$ cm^3 aerosol/cm^3 air[15,35]), equilibrium uptake due to solubility alone will not provide an appreciable sink for gaseous methanol (≤ 0.02%).

Heterogeneous reaction between methanol and sulfuric acid does occur and may provide a pathway for accumulation of organic species in ambient particles. If formed, mono- and dimethyl sulfate (CH_3OSO_3H, $CH_3OSO_3CH_3$) are significantly more soluble than methanol in H_2SO_4 ($H^* \sim 10^{10} - 10^{11}$ M atm^{-1}, estimated from Hansen et al.[36]), leading to possible accumulation of organic sulfates in stratospheric particles. At 12 km with $T = 219$ K and ∼10% ambient relative humidity

(RH), such as might be seen in the tropics[37] outside regions of convective influence or at higher latitudes where 12 km is above the tropopause, sulfuric acid aerosols would have a concentration near 60 wt %.[38] An estimate of $k \sim 10^{-12}$ s^{-1} indicates the reaction is much too slow to occur on atmospheric time scales at cold temperatures commonly found at this altitude, even under the dry conditions illustrated here. At higher relative humidity, the aerosols will take up additional water and become more dilute, reducing the rate further.

However, at warmer temperatures, the rate could be faster. At ~ 5 km with $T = 267$ K and RH = 30%, unneutralized sulfuric acid aerosols would have a composition of approximately 50 wt %, and k could be as large as $\sim 10^{-8}$ s^{-1}. Drier conditions, such as in the layers with relative humidity as low as 5% sometimes seen during the INDOEX field mission[39] or in midlatitude tropopause folds,[40] would generate aerosols of ~67 wt % H_2SO_4 and $k \sim 10^{-7}$ s^{-1}. Presuming the equilibrium solution concentration of methanol is maintained, this leads to a rate of $\sim 10^{-12}$ mol L^{-1} s^{-1} for the buildup of organic products in aerosol particles. If dry, reactive conditions were maintained for 3 days, solution concentrations of CH_3OSO_3H could reach $\sim 1.5 \times 10^{-6}$ M, or approximately one molecule per particle. Clearly, that concentration is too low to suggest that monomethyl sulfate is the dominant organic species detected by field measurements. Thus, if the estimates of rate coefficients made here are correct, the formation of CH_3OSO_3H from methanol reaction in aqueous sulfuric acid solution is unlikely to be the source of the ubiquitous organic material observed in sulfate aerosols in the UT/LS.[3,5]

To verify that uptake and reaction are also too slow to deplete gaseous methanol, we find an effective k_{het} for loss from the gas phase due to reactive uptake:

$$\text{rate} = k_{het} n_g = JS = \frac{\gamma n_g \bar{c} S}{4} \tag{7}$$

where J is the flux of molecules to aerosol surfaces (molecule cm^{-2} s^{-1}) and S is the surface area density (cm^2 particle per cm^3 air). Using $D = 9 \times 10^{-7}$ cm^2 s^{-1} and $k = 1 \times 10^{-7}$ s^{-1}, the reacto-diffusive length ($l = \sqrt{D/k}$) is found to be 3 cm. As this is much larger than the typical sulfate particle radius (r = 0.1 μm), methanol will diffuse throughout the particle and reaction will take place in the entire volume. Thus, assuming the accommodation coefficient (α) is unity, the steady-state reactive uptake coefficient is calculated from

$$\gamma = \frac{4H^*RTkr}{3\bar{c}} \tag{8}$$

where r is the particle radius and k is the solution-phase rate coefficient discussed above. Therefore,

$$k_{het} = \frac{\gamma \bar{c} S}{4} = \frac{H^*RTkrS}{3} \tag{9}$$

with $H^* = 2.4 \times 10^4$ mol L^{-1} atm^{-1}, $T = 267$ K, $k = 1 \times 10^{-7}$ s^{-1}, $r = 10^{-5}$ cm, and $S = 2 \times 10^{-8}$ cm^2 cm^{-3},[35] $k_{het} = 3.5 \times 10^{-15}$ s^{-1}. This value is much smaller than the rate coefficient for the dominant gas-phase loss via reaction with OH ($k = 7 \times 10^{-7}$ s^{-1} when OH = 1×10^6 cm^{-3} and k_{II} (267 K) = 7×10^{-13} cm^3 molecule^{-1} s^{-1}),[41] indicating very little contribution of this heterogeneous reactive process to the overall loss of methanol from the gas phase. Thorough treatment due to the large reacto-diffusive length relative to particle size[42] and a possible value of $\alpha < 1$ will further reduce this rate for the heterogeneous loss of methanol via reaction with H_2SO_4.

Conclusions

The effective Henry's law coefficient, H^*, for methanol in sulfuric acid solutions has been measured over the range 197–231 K. For solutions between 45 and 72 wt % H_2SO_4, solubility increases with decreasing temperature and increasing acidity, with values ranging from 10^5 to 10^8 M atm^{-1}. A parameterization is given (eqs 3, 4, and 6, with $\Delta S = -134$ J mol^{-1} K^{-1}) for calculation of the temperature-dependent H^* as a function of sulfuric acid composition.

Using the measured solubilities, we find that ≤ 0.02% of gaseous methanol will partition into UT/LS aerosols. Subsequent reaction of methanol with sulfuric acid is too slow to enhance this uptake appreciably. Thus, the interaction of methanol with sulfate aerosols will not deplete gas-phase CH_3OH or produce significant quantities of condensed-phase organic material. Neither the imbalance in the global methanol budget nor the origin of organics in UT/LS aerosols can be explained via the interaction of methanol with sulfate particles. Further study is clearly necessary for the resolution of these issues.

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Appendix: Previous Kinetic Studies of Methanol Reaction in Aqueous H_2SO_4

Vinnik et al.[23] reported nuclear magnetic resonance studies of the kinetics of methanol reaction with D_2SO_4 at 298 K. They found that the rate of esterification increased with increasing acidity, with the first-order rate constant at 71 wt % equal to 2.8×10^{-4} s^{-1}. This is consistent with the previous work of Deno and Newman[22] and Clark and Williams.[32] The former found a second-order rate constant of 69×10^{-7} s^{-1} (mol/1000 g solution)$^{-1}$ for equimolar methanol in 70.4 wt % H_2SO_4 at 298 K ($k_1 = 4.5 \times 10^{-5}$ s^{-1}) and 30×10^{-7} s^{-1} (mol/1000 g solution)$^{-1}$ ($k_1 = 1.8 \times 10^{-5}$ s^{-1}) for ethanol under identical conditions. Clark and Williams[32] did not study methanol, but their value for ethanol in 70 wt % H_2SO_4 at room temperature ($k = 4.3 \times 10^{-5}$ s^{-1}) is comparable to that of Deno and Newman.[22]

In addition, Clark and Williams[32] measured $k_{ethanol}$ at 273 K, allowing some estimate of the temperature dependence to be made. Using their A-factor and activation energy for reaction of ethanol in 70 wt % H_2SO_4 ($A = 0.1 \times 10^{13}$ s^{-1}; $E = 22.3$ kcal mol^{-1}), we can estimate the rate of methanol esterification under our most reactive low-temperature conditions (72 wt % H_2SO_4, 221 K). For ~70 wt % H_2SO_4 at 221 K, ethanol in H_2SO_4 should have rate constant of $\sim 9 \times 10^{-11}$ s^{-1}. Using Deno and Newman's[22] ratio of 4.5:1.8 for methanol:ethanol rates suggests $k \leq 2.3 \times 10^{-10}$ s^{-1} for methanol in our experiments.

Very recently, Kane and Leu[43] reported values closer to k = 0.1–10 s^{-1} for CH_3OH in 65–80 wt % H_2SO_4 solutions. The evidence presented by those authors for reaction of methanol with sulfuric acid at low temperatures is the lack of complete desorption of methanol from their coated-wall flow tube after exposure to a sulfuric acid sample. In our studies, we have occasionally monitored desorption following uptake, and we find that a single desorption burst which decays to levels near background can be followed by successive bursts if the system is allowed to reequilibrate (isolated from pumping) between cycles. From this observation, we suggest that diffusion limitations and depletion of the surface layer of Kane and Leu's H_2SO_4 solutions may have influenced the amount of methanol detected.

For their highest concentrations of H_2SO_4, it is also possible that reaction occurs during the heating ramp. As temperature is increased, the solubility of methanol decreases and more desorption should occur, as was observed. However, the reaction rate is also increased.[32] Estimates of $k = 9.3 \times 10^{-5}$ s^{-1} for 81 wt % and $k = 1.9 \times 10^{-3}$ s^{-1} for 93 wt % H_2SO_4 at 273 K[32,22] would give 1/*e* lifetimes of ∼100 and ∼10 min, respectively. In these cases, the length of the ramp used (∼15 min with $T \geq$ 273 K) and subsequent observation time (∼20 min) could allow a measurable fraction to react as the temperature was increased.

For these two reasons, we believe that the "fraction desorbed" reported by Kane and Leu may not necessarily indicate reaction of methanol in H_2SO_4 at the uptake temperature.

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