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**MEASUREMENT OF THE SOLUBILITY
OF METHYL SALICYLATE
IN AQUEOUS DROPLETS**

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PREFACE

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MEASUREMENT OF THE SOLUBILITY OF METHYL SALICYLATE IN AQUEOUS DROPLETS

1. INTRODUCTION

Methyl salicylate (MS), commonly known as oil of wintergreen, is a physical and chemical simulant for mustard gas (agent HD). MS simulates the solubility of HD in the aqueous phase as well as its reactivity to water. For this reason, the simulant is widely used in design studies that investigate the use of water for the removal and decontamination of HD. One such study involves the use of water aerosols to accelerate the vapor purge rate of current NBC shelter airlocks.

In the referenced study, filter air was used to purge vapors from a shelter airlock contaminated by entering personnel. With purge air only, it normally took 5 min to reduce the vapor concentration to an acceptable level, and this severely limited the personnel transfer rate through the airlock. By introducing a fine water spray into the airlock, the personnel transfer rate was increased by as much as a factor of two. Operationally, the water spray characteristics and the purge airflow rate were parametrically varied to optimize the vapor removal process. To separate the vapor removal contributions due to aerosol from that of the purge gas, it was necessary to have knowledge of the fundamental kinetics and thermodynamics of vapor absorption by aqueous droplets. Due to the paucity of experimental data on vapor absorption by aerosols, the investigators relied heavily on data derived from bulk studies to estimate the kinetics and thermodynamics of aerosols. This approach can lead to significant errors when the aerosol thermodynamics are influenced by curvature effects (Kelvin's law). To support these vapor removal studies, kinetic and thermodynamic data were established for individual aerosol droplets that are immersed in a reactive vapor environment.

In this report, a technique is presented for measuring *in situ* the kinetics and thermodynamics of individual droplets exposed to reactive vapors. The technique is referred to as single-particle, electrodynamic balance,² and uses both static and oscillating electric fields to suspend single droplets in flowing gases. The particle can be interrogated optically and gravimetrically using lasers and voltage sources that maintain the droplet at the center of a focusing electrodynamic field. In this report, the absorption kinetics and thermodynamics of the single droplet are determined from the weight changes in the droplet as it is exposed to the reactive vapors. Small droplet weight changes are detected from the adjustments in the static electric field that is required to maintain the droplet at the center of the field focusing.

The absorption efficiency of MS by aqueous droplets of phosphoric acid and water is studied as a function of acid concentration. It is shown that MS exhibits a minimum solubility of 0.11% at an acid concentration of 62 Wt % acid, and the solubility rapidly increases for acid concentrations below and above this value. The kinetics of MS vapor absorption is a diffusion-controlled, gas phase and is not limited by internal liquid-phase diffusion. Evidence of liquid phase hydrolysis of MS is found from the gravimetric measurements, and the hydrolysis rates are consistent with earlier studies.⁵

2. EXPERIMENTATION

Electrodynamic suspension of single droplets has proven to be a valuable tool in investigating a wide range of phenomena in aerosol physics. The principle for droplet suspension is based on developing a phase lag between the droplet motion and the oscillating electric field. For linear electric fields, the droplet experiences a net time-averaged force that opposes the weight of the droplet. In addition, if a static electric field that exactly balances

the particle weight is impressed across the chamber, the droplet remains stationary at the null point of the oscillating field.

Figure 1 shows a schematic of the electrodynamic droplet suspension chamber, approximately 60 cm³ in volume and the associated electro-optical circuitry. The static electric field is established by impressing a voltage differential across the top and bottom electrodes that are electrically insulated from the central electrode. An oscillating voltage of 500-1000 V is applied to the central electrode that establishes a linear electric field inside the chamber and provides the appropriate restoring force for the charged droplet. As the droplet weight changes, the static voltage differential is changed to maintain the droplet at the null point of the chamber.

Charged phosphoric acid droplets are generated by applying a high voltage to a capillary tube that contains the acid. At a critical voltage, a spray of charged droplets is generated, and they are guided into the chamber using focusing fields. All droplets except one are removed from the chamber. The droplet is accurately positioned at the electrodynamic null point by monitoring the light scattered by the droplet at 90 ° (Figure 1a). Light from a 2-mW helium-neon laser (6328-Å wavelength) is targeted onto the droplet, and the light scattered at 90 ° is detected with a split photodiode. The split photodiode consists of two diode panels that independently respond to the light scattered by the droplet. The signal from the two diodes is passed through a difference/sum amplifier that outputs into a digital multimeter. If the droplet is positioned at the null point, then the difference output reads zero. If the droplet moves up or down, the difference output will be nonzero, and the static voltage is automatically adjusted by a proportional-integral-derivative (PID) circuit that brings the difference output back to zero. The time-dependent balancing voltage is recorded on a quartz-drive recorder.

The relative humidity (RH) of the chamber and concomitantly the acid concentration of the droplet is varied by introducing a gas, preconditioned to a set RH, at 1 atmosphere of pressure. The RH of the gas is accurately controlled by mixing water-saturated air with dry air at known proportions. MS vapor is introduced by bubbling dry air through liquid MS and then mixing the MS vapor-saturated air with the water-saturated air. A given experiment is initiated by introducing a single phosphoric acid droplet into the chamber. The droplet size is determined using an image splitter in combination with a 35-mm objective. In the present set of experiments, the droplet diameter was approximately 50 μm. After equilibrating the droplet with the chamber RH, the droplet balancing voltage was monitored for stability. If the droplet voltage remained constant for 10 min, the MS vapor was introduced to the chamber, and the voltage dynamics was measured.

3. RESULTS

Figures 2 and 3 show the characteristic change in the droplet balancing voltage as MS vapor is introduced into the chamber. Initially, the balancing voltage rapidly increases, indicating a corresponding increase in the droplet weight as MS vapor is absorbed by the droplet. After approximately 2 min, the balancing voltage reaches a maximum and begins to decrease at a rate slower than the initial growth phase. The voltage decrease continues for 10 min, after which the balancing voltage stabilizes at a value that exceeds the original balancing voltage of the droplet.

As shown in Figures 2 and 3, RH has a pronounced effect on the voltage dynamics of individual phosphoric acid droplets as MS vapor is introduced into the chamber. In each case, the droplet voltage exhibits an initial growth phase that is followed by a slower decay phase. As the RH increases, the maximum increase in the voltage decreases, until at a RH of 50%,

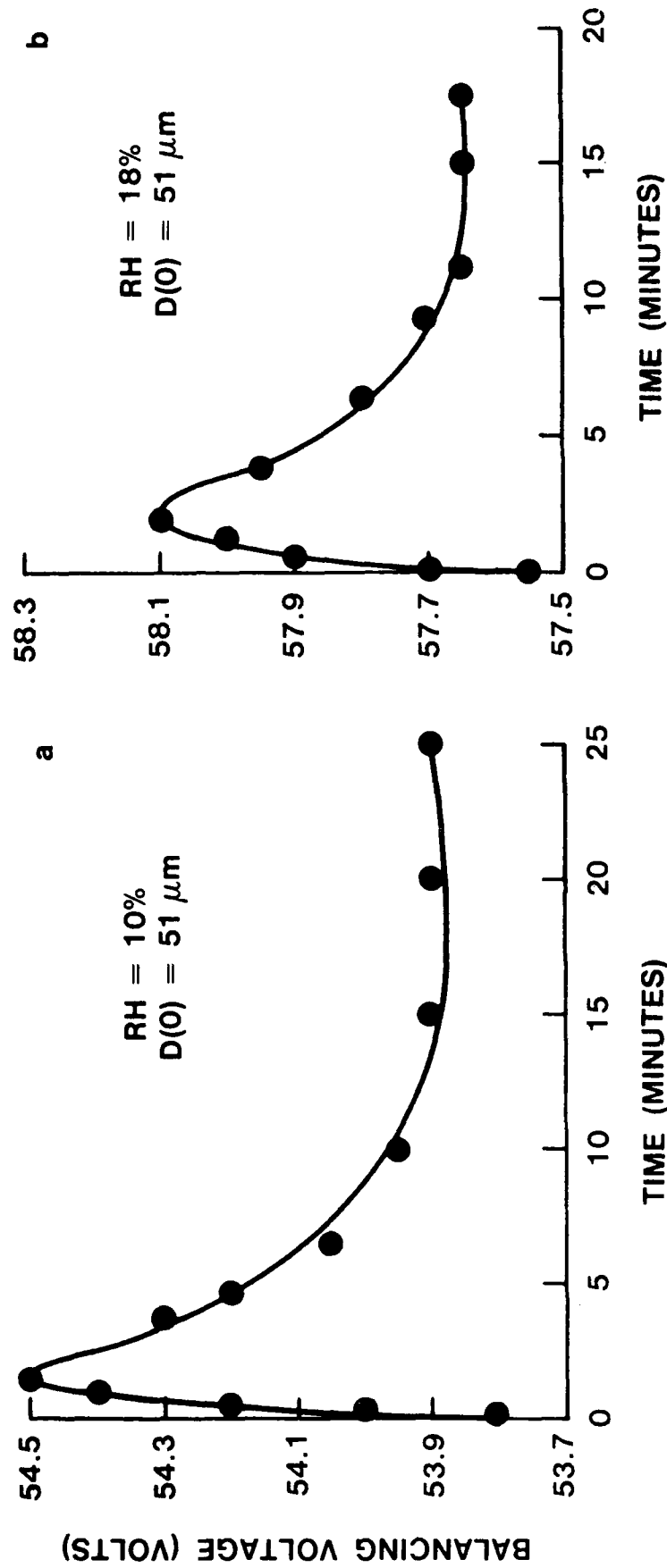
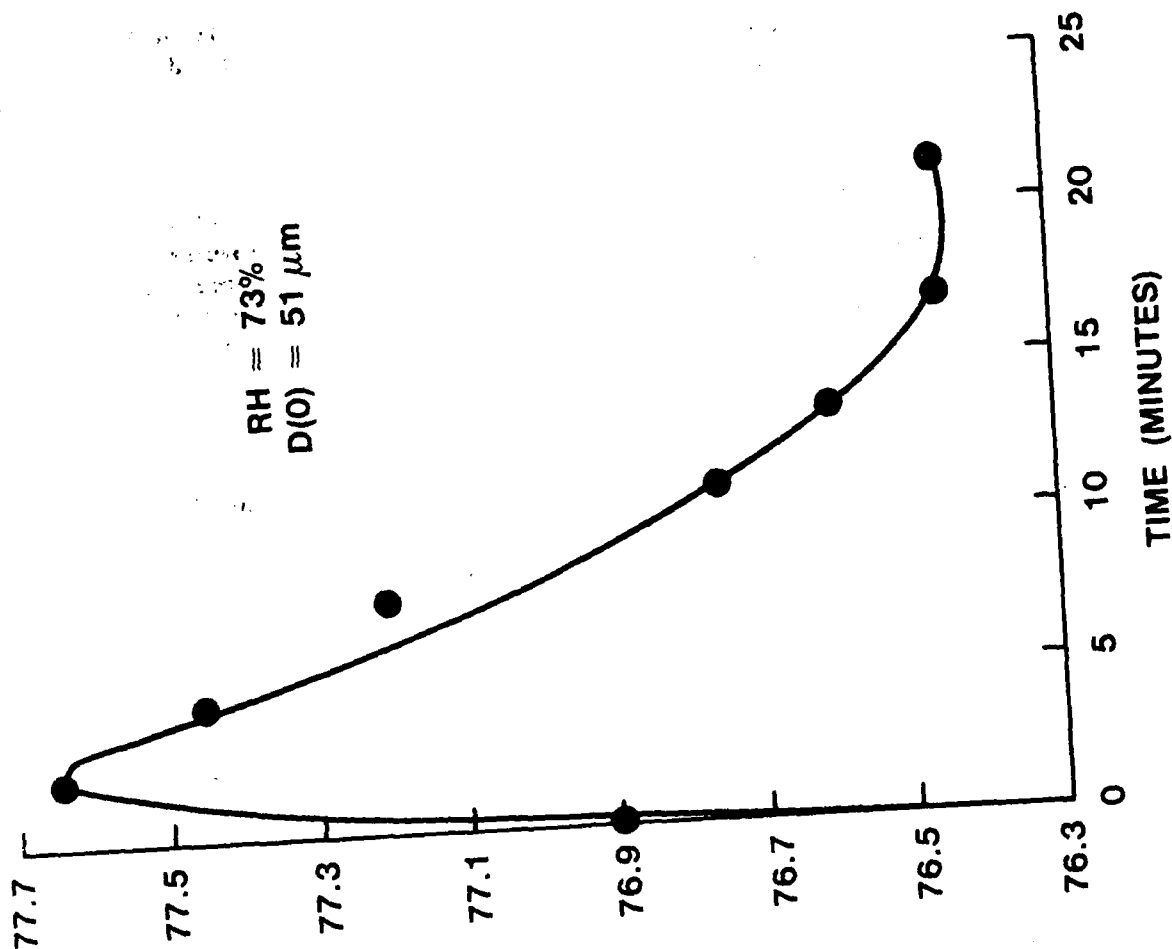


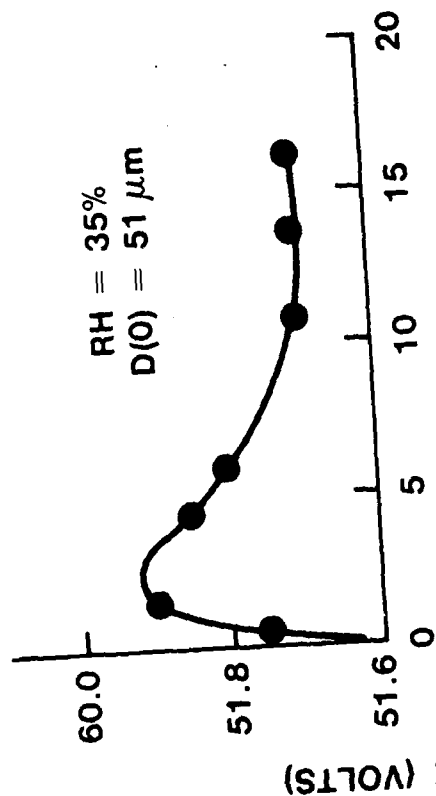
Figure 2. Suspension Voltage Change of an Aqueous Droplet Due to the Absorption of MS Vapors - Low Relative Humidity

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a



b

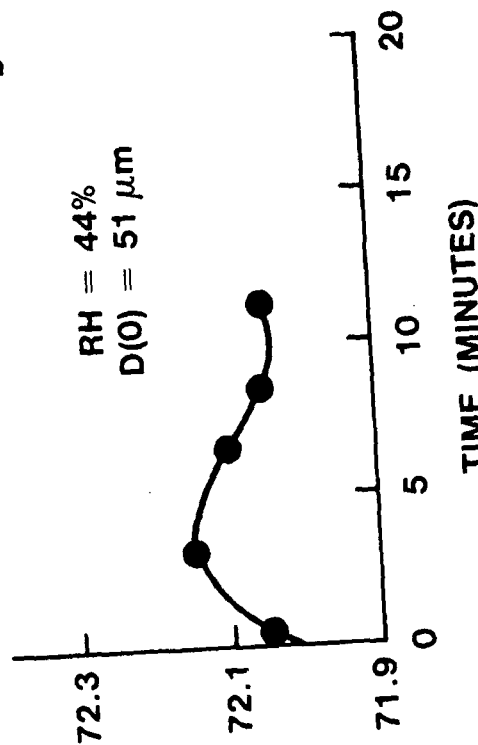


Figure 3. Suspension Voltage Change of an Aqueous Droplet Due to the Absorption of MS Vapors - High Relative Humidity

the maximum voltage reaches a minimum. As the RH increases further, the maximum voltage once again increases. Concomitantly, the time required for the droplet voltage to decay to a specific fraction of its original value is independent of the RH.

4. DISCUSSION

A consequence of single particle trapping by focusing electrodynamic fields is that the balancing voltage is proportional to the particle mass. With that knowledge, Figures 2 and 3 are reinterpreted as showing that the aqueous droplet initially experiences a rapid weight increase as the MS vapor is introduced. The weight increase must be due to the absorption of MS vapor by the aqueous droplet. After a minute or so, the droplet weight begins to decrease, but now at a rate decidedly slower than the earlier growth phase.

4.1 MS Solubility.

The solubility of MS in the aqueous droplet is computed from the relative balancing voltage in the following manner. The total droplet mass m_d is given by:

$$m_d = m_a + m_w + m_{ms} \quad (1)$$

where a is acid, w is water, and ms is methyl salicylate. Assuming that MS absorption does not effect the mass of water or acid, the relative mass increase is given by:

$$\frac{m_d(f)}{m_d(i)} = \frac{V(f)}{V(i)} = \frac{m_a + m_w + m_{ms}}{m_a + m_w} \quad (2)$$

From equation 2 the weight percentage of MS in the droplet is expressed in terms of the relative balancing voltage as:

$$\text{Wt \% MS} = (1 - V(i) / V(f)) \quad (3)$$

From the droplet voltage data at maximum increase, the MS solubility in the aqueous phosphoric acid droplets is computed as a function of RH.

Table 1. Dependence of MS Solubility
on Relative Humidity

MS (Wt %)	RH (%)
1.211	10
0.912	18
0.539	35
0.291	44
0.110	50
0.485	60
1.687	73

Table 1 shows that the solubility of MS in aqueous phosphoric acid droplets exhibits a minimum at 50% RH and increases rapidly for decreasing and increasing RH. The magnitude of the MS solubility exceeds previously reported values³ by 50% at 50% RH to more than an order of magnitude at RH of 10 and 73%. An explanation does not exist at this time for this functional dependence of the MS solubility on the RH. However, it is interesting to note that previous researchers⁴ have found that the specific electrical conductivity of phosphoric acid solutions shows a similar functional dependence. Specifically, the electrical conductivity reaches a maximum at 50% phosphoric acid and decreases for increasing and decreasing acid concentration. One could draw a correlation from this data and tentatively conclude that a large electrical conductivity leads to a low MS solubility. If one further associates a large conductivity with a high degree of acid ionization, then it can finally be asserted that it is the high degree of phosphoric acid ionization that inhibits MS solubility in the aqueous phase.

The author observed a similar behavior⁵ in studying the dependence of monomolecular cohesion on suphase acidity. The acid ionized the surfactant molecules, and this lead to intermolecular repulsion that reduced the surface density of surfactant molecules. It could be postulated that the MS molecules are ionized by the acid molecules, and this leads to a reduced solubility in the aqueous solution. However, while this hypothesis seems plausible, the maximum in the phosphoric acid solution electrical conductivity is not quite in phase with the minimum of the MS solubility. To more clearly see this, the data in Table 1 is reformatted in terms of the weight percentage of acid. This is achieved by using well established water activity relationships for phosphoric acid solutions.² Table 2 shows the dependence of electrical conductivity and weight percentage of MS on the acid concentration.

Table 2. Dependence of Electrical Conductivity and MS Solubility on Acid Concentration

MS (Wt %)	Electrical Conductivity (mhos)	Acid (Wt %)
-	0.0566	10
-	0.1129	20
-	0.1654	30
1.687	0.2010	48
0.485	-	57
0.110	-	62
0.539	-	70
-	0.1209	75
0.912	-	80
1.211	0.0780	85

As shown in Table 2, the minimum in the MS column occurs in a region where the data on electrical conductivity is lacking. It can be concluded from the data that the maximum in the electrical conductivity occurs between 48 and 75 Wt % acid, and the weight percentage of MS may in fact be 180° out of phase with the electrical conductivity. Approximate interpolation of the conductivity data suggests that the maximum conductivity occurs at 57 Wt % of acid, and this is slightly out of phase with the minimum in the weight percentage of MS.

4.2 Corrected MS Solubility.

As stated earlier, the solubility values for MS in the aqueous droplets are considerably larger than those values previously reported for bulk systems. One possible explanation for this discrepancy in MS solubility is that the total droplet weight change is the result of MS and water absorption. That is, as the MS vapor is absorbed by the droplet, the MS acts to depress the water activity in the acid droplet. This is commonly referred to as Raoult's law for dilute solutions. For the droplet to reequilibrate with the existing RH, it must absorb water from the gas until the droplet water activity matches its original value. Therefore, if the droplet weight change is attributed solely to MS vapor absorption, the solubility of MS in the droplet would be overestimated. To correct the MS solubility values due to water absorption, data is required on the water activity of MS in aqueous phosphoric acid solutions. Because this data is not available, the water activity of the MS, water, and acid system is heuristically modeled in the following manner.

It is assumed that the MS and phosphoric acid molecules are described by the same free energy potentials, and so the water activity of the MS and acid system can be modeled by well-established, phosphoric acid, water-activity data. Subject to this assumption, the value of the MS solubility corrected for water absorption can be written as (see appendix):

$$\text{Wt \% MS (corrected)} = \frac{g(RH)}{100} (1 - V(i)/V(\infty)) \quad (4)$$

where $g(RH)$ is the percentage of acid as a function of RH in the phosphoric acid and water system. Thus, the corrected MS solubility differs from the uncorrected value by a scale factor that represents the percentage of acid at a given RH. As the RH increases, the percentage of acid and the scale factor decrease. Consequently, the effect of the scale factor is to reduce the value of the uncorrected solubility at the higher RH. This is to be expected, because water absorption effects become pronounced at the higher RH. Table 3 shows the corrected MS solubility as a function of acid concentration.

Table 3. Corrected MS Solubility
as a Function of Acid Concentration

MS (Wt %)	Acid (Wt %)
1.032	85
0.725	80
0.377	70
0.190	65
0.068	62
0.275	57
0.816	48

Table 3 shows that the MS solubility still exhibits a minimum at 62 Wt % acid and that the minimum value is in excellent agreement with previous literature bulk values. Nevertheless, the MS solubility still exceeds bulk values by more than an order of magnitude at dilute and concentrated acid levels. Thus, it is concluded that water absorption effects cannot account for the functional dependence of the MS solubility on the weight percentage of acid and the large disparities between the solubilities reported in this work and those values reported for bulk systems.

4.3 Hydrolysis.

Because the RH and MS partial pressure are held constant during the duration of the experiment, it is concluded that the droplet weight loss is due to the release of volatiles formed by the hydrolysis of MS in the aqueous droplet. MS undergoes degradation by hydrolysis under acidic or alkaline conditions [6]. Hydrolysis of the ester produces methyl alcohol and salicylic acid. It is asserted that the droplet weight loss is due to the evaporation of methyl alcohol and the volatile salicylic acids. The assertion that the droplet weight loss is the result of MS hydrolysis is supported by the observed decay times in the droplet weight. Previous researchers have found that the half-life of the agent HD is approximately 5 min at 25 °C [3], and this is consistent with the droplet weight decay times observed in Figures 2 and 3. Furthermore, it has been shown that the hydrolysis reaction is first order in the MS concentration [3]. Comparing Figures 2 and 3, it is seen that the half-life of the absorbed vapor is independent of the initial amount of MS absorbed, a characteristic of a first order reaction. The initial growth dynamics of the droplet are rapid, normally requiring 1 min to complete. This growth time is characteristic of gas-phase, diffusion-controlled growth, and this demonstrates that the vapor-absorption process is not liquid-phase, diffusion controlled.

5. CONCLUSIONS

The absorption of MS vapor by individual aqueous droplets has been measured for the first time. The absorption dynamics are measured *in situ* and in real time. Using newly developed single particle trapping technology in combination with an electro-optical, automatic-particle stabilization circuit, the solubility of MS vapor in aqueous droplets of phosphoric acid and water is measured as a function of acid concentration at 25 °C. It is shown that the MS solubility in the aqueous droplet can be an order of magnitude greater than that value previously reported for bulk systems. The solubility exhibits a minimum value of 0.068% at 62 Wt % acid and rapidly increases for dilute and concentrated acid levels. Evidence of MS hydrolysis in the droplet is presented, and characteristic half-lives agree with values previously found for bulk systems.

6. RECOMMENDATIONS

As a result of this study, the following actions are recommended:

- Conduct aerosol chamber tests to measure the absorption efficiency of a cloud of phosphoric acid droplets or an equivalent phosphorus smoke immersed in MS vapor. Measure the absorption efficiency as a function of relative humidity.
- Measure the chamber vapor concentration of methyl alcohol and salicylic acid *in situ* and in real time to detect the hydrolysis of MS in the aerosol droplets.
- Initiate experiments on the effect of additives such as boric acid on the solubility of MS in aqueous droplets.

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APPENDIX

MS SOLUBILITY CORRECTED FOR WATER ABSORPTION EFFECTS

The water activity of the phosphoric acid and water system is given by

$$a_w = 6.159 \times 10^{-6} p^3 - 1.2119 \times 10^{-3} p^2 + 6.119 \times 10^{-2} p - 7.511 \times 10^{-2} \quad (\text{A-1})$$

where $p = m_a \times 100 / (m_a + m_w)$.

If it is assumed that the free energy potentials for MS and phosphoric acid are identical, then equation A-1 still holds with a new "acid" concentration defined as

$$p = \frac{m_a + m_{ms}}{m_a + m_w + m_{ms}} \times 100 \quad (\text{A-2})$$

Equation A-1 can be inverted to give

$$p = g(RH) = 65.97 + 64.5 \cos[\cos^{-1}(2.421 RH / 100 - 1.030) / 3 + 240] \quad (\text{A-3})$$

Substituting Equation A-2 into Equation A-3 gives

$$(1 - g(RH) / 100) m_a = (g(RH) / 100 - 1) m_{ms} + g(RH) / 100 m_w \quad (\text{A-4})$$

The total voltage change in the droplet is due to water and MS absorption and is written as

$$(V(f) / V(i) - 1) m_o + = m_{ms} + m_w^* \quad (\text{A-5})$$

where m_o is the original droplet mass and m_w^* is the water mass added to the droplet due to MS absorption. The water added is the difference between final and original amounts of water and Equation A-5 is rewritten as

$$m_w = (V(f) / V(i) - 1) m_o - m_{ms} + m_{wo} \quad (\text{A-6})$$

Equations A-4 and A-6 constitute two equations with two unknowns and can be solved to give

$$m_{ms} = g(RH) / 100 [(V(f) / V(i) - 1)m_o + m_{wo}] + (g(RH) / 100 - 1)m_a \quad (A-7)$$

Substituting Equations A-6 and A-7 into Equation A-2, the corrected MS solubility is given by

$$\text{Wt \% MS (corrected)} = g(RH) / 100 (1 - V(i) / V(f)) \quad (A-8)$$