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Sarah D. Brooks

University of Colorado, Boulder

Matthew E. Wise

University of Colorado, Boulder, mawise@cu-portland.edu

Melinda Cushing

University of Colorado, Boulder

Margaret A. Tolbert

University of Colorado, Boulder

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Deliquescence behavior of organic/ammonium sulfate aerosol

Sarah D. Brooks, Matthew E. Wise, Melinda Cushing, and Margaret A. Tolbert

Department of Chemistry & Biochemistry and CIRES, University of Colorado, Boulder, USA

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[1] Recent studies have shown that tropospheric aerosols composed of internal mixtures of organics with sulfates are quite common with the organic composing up to 50% of the particle mass. The influences of the organics on the chemical and physical properties of the aerosol are not known. In this paper, we report the solubility of a series of dicarboxylic acids in saturated ammonium sulfate solution as a function of temperature. We also report the deliquescence relative humidity (DRH) of the pure dicarboxylic acids and of mixtures of dicarboxylic acids with ammonium sulfate. For the systems studied, we find that the presence of water-soluble dicarboxylic acids caused deliquescence to occur at a lower relative humidity (RH) than pure ammonium sulfate. In contrast, the less soluble dicarboxylic acids had no measurable effect on the deliquescence relative humidity of ammonium sulfate. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry. **Citation:** Brooks, S. D., M. E. Wise, M. Cushing, and M. A. Tolbert, Deliquescence behavior of organic/ammonium sulfate aerosol, *Geophys. Res. Lett.*, 29(19), 1917, doi:10.1029/2002GL014733, 2002.

1. Introduction

[2] The chemical reactivity and cloud nucleating ability of aerosols depends, in part, on the aerosol phase. While the deliquescence (water uptake to form a solution) and efflorescence (water loss to form a crystal) of pure ammonium sulfate is well established [e.g., Martin, 2000; Onasch *et al.*, 1999], recent field data shows evidence that aerosols may be composed of up to 50% or more organic material [Murphy *et al.*, 1998]. A significant portion of the total organic content of the tropospheric aerosol has been identified as water-soluble organics, including dicarboxylic acids [Saxena and Hildemann, 1996]. The deliquescence and efflorescence RH's of these mixed composition particles are not known.

[3] Pure ammonium sulfate makes the transition from a solid to a liquid at a characteristic deliquescence relative humidity (DRH) of 80% at room temperature. It has been shown that the DRH of ammonium sulfate in the presence of another electrolyte will always be lower than the DRH of the ammonium sulfate alone [Wexler and Seinfeld, 1991]. Recently, Clegg *et al.* [2001] have modeled the deliquescence of a few multicomponent solutions of inorganic electrolytes and organic molecules at 298.15 K. They find that the presence of weakly dissociating organic compounds also lowers the deliquescence RH of the inorganics.

[4] In a mixed system, the lowest humidity at which the two components can mutually go into solution is defined as the eutonic DRH. The ratio of one component to the other in solution at this RH is the eutonic composition. Theory predicts that other mixed compositions will take up some water at the DRH of the eutonic, while some solid will remain in the solution until the RH is increased to the DRH of the composition of interest, where the system becomes fully deliquesced and no solids remain.

[5] We have determined the solubilities, eutonic compositions, and DRH's of eutonic mixtures of dicarboxylic acid/ammonium sulfate at temperatures ranging from 24 °C to −10 °C. At 24 °C, we have also determined the DRH's of mixtures of a range of organic/sulfate compositions. The organic compounds studied are the C-2 to C-6 dicarboxylic acids, as well as maleic and l-malic acid. The DRH we report refers to full deliquescence rather than the onset of water uptake.

2. Experimental

[6] The bulk property measurements were conducted using a sealed test tube containing 10 ml of solution placed in a cooler and kept at a constant temperature by a circulating methanol bath. We monitored the temperatures of the solution, the gas above the solution, and the surrounding coolant bath with thermocouples. At the coldest temperature, −10 °C, the temperature gradient between the solution and gas above in the worst case was 0.55 °C, corresponding to an error in RH of 2.25%. To measure the DRH, a saturated solution of either pure ammonium sulfate, pure organic, or a solution saturated with respect to both ammonium sulfate and organic was prepared and allowed to equilibrate overnight. The relative humidity above the solution at the given temperature was then measured using a Control Company RH meter. The uncertainty in measurement of RH up to 95% was $\pm 3\%$, based on temperature gradients and instrumental uncertainty. Since the RH meter is not rated for values above 95%, we report any measurements of higher relative humidities as $\geq 95\%$.

[7] To determine the eutonic composition we started with a saturated solution of ammonium sulfate in which one crystal of undissolved ammonium sulfate was present. To this solution aliquots of the organic were added until the solution was saturated with respect to the organic and one crystal of organic was present. Since the presence of the organic increased the solubility of ammonium sulfate in water, the crystalline ammonium sulfate often dissolved, in which case more ammonium sulfate was added until the solution was saturated with respect to ammonium sulfate once again. This procedure was continued until crystals of both ammonium sulfate and organic were present, indicating that the solution was saturated with respect to each of its components. We were able to visually distinguish between the crystals since solid ammonium sulfate crystals are cubic

Table 1. Solubilities of Dicarboxylic Acids in Water

	Solubility (Wt%)		
	24 °C	9 °C	4 °C
Water soluble compounds			
Malonic acid, $\text{CH}_2(\text{CO}_2\text{H})_2$	62.2 (61.7) ^a	56.1	51.7
Glutaric acid, $\text{HO}_2\text{C}(\text{CH}_2)_3\text{CO}_2\text{H}$	60.3 (54.0)	44.8	35.0
Maleic acid, $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$	41.3 (44.6)	36.7	30.1
L-Malic acid, $\text{HO}_2\text{CCH}_2\text{CH}(\text{OH})\text{CO}_2\text{H}$	72.3 (59.1)	68.6	40.8
Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$	43.4 (42.8)		40.8
Less soluble compounds			
Oxalic acid, $\text{HO}_2\text{C}-\text{CO}_2\text{H}$	11.2 (10.7)		1.0
Succinic acid, $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CO}_2\text{H}$	8.7 (8.09)		2.3
Adipic acid, $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CO}_2\text{H}$	2.5 (2.4)		1.0

^a Values in parenthesis are taken from *Perry*, 1941.

and translucent, while most of the organics in this study are powdery white solids. Estimated errors in the eutonic compositions were approximately $\pm 1 \times 10^{-2}$ molar ratio for the water soluble organics and $\pm 1 \times 10^{-3}$ molar ratio for the less water soluble organics based on the amounts of material added with the last aliquot before saturation.

[8] To confirm that we had correctly determined the composition of the eutonic, we made solutions with a large excess of each compound. At room temperature, 24 °C, we measured the RH of the measured eutonic solution as well as the solutions prepared with large excess solids. Within error, the DRH's were in agreement showing that we had, in fact, determined the highest solubilities and lowest DRH for each mixed system.

[9] To check for mixed solid phases, we reversed the procedure and prepared an organic solution and then added ammonium sulfate. In all cases, we found that the maximum solubility of each component in the mixed solutions was not dependent on the order in which the components were added. Furthermore, the measured DRH for eutonic solutions prepared by each method were the same within error. Hence, we conclude that no mixed solid phases formed in the systems studied.

[10] At room temperature we also determined DRH for mixed water-soluble organic/ammonium sulfate solutions of higher and lower organic weight ratio than contained in the eutonic proportions. Estimated errors for non-eutonic compositions were approximately 0.005 molar ratio. In non-eutonic cases, by preparing solutions either saturated with respect to ammonium sulfate or saturated with respect to the organic, we ensure that we are measuring DRH for a system of the specified composition.

3. Results and Discussion

[11] The solubilities of the pure organic compounds in water at room temperature are well known and are summar-

ized in Table 1 [*Perry*, 1941]. Here we measured the solubilities in water at 24, 9, and 4 °C. We find reasonable agreement between our measured solubilities of dicarboxylic acids in water and the literature values. Interestingly, the saturated dicarboxylic acids with an even number of carbons are much less soluble in water than those acids with an odd number of carbons. As indicated in Table 1, the solubility in water decreases as the temperature decreases. For the more soluble compounds, we attempted to measure the solubility at -10 °C, but the glutaric, L-malic acid, and maleic acid solutions froze. We do not report the solubility of malonic acid -10 °C, since a saturated solution was made at a higher temperature, and significant amounts of the acid precipitated out of solution during the cooling process.

[12] In addition to the solubilities of the organic compounds in water, we measured the solubilities in saturated ammonium sulfate to determine the eutonic composition. These are indicated in Table 2. In Table 2, the mole fraction organic is defined as the moles of organic divided by the total moles of organic, ammonium sulfate, and water in the sample. The eutonic composition varies from mainly ammonium sulfate to mainly organic depending on the organic compound. In all cases, the organic mole fraction in the eutonic composition decreases as the temperature decreases.

[13] Since the Kelvin effect on DRH is insignificant for particles of 0.05 μm or larger in radius [*Dufour and Defay*, 1962], the DRH of an aerosol system with particle sizes larger than this can be predicted by bulk thermodynamics. Since the relative humidity of a saturated solution is equivalent to the DRH of an aerosol of the same composition, experiments conducted on bulk solutions can be used to predict the DRH of aerosol systems. To confirm this, we measured the RH over a saturated solution of pure ammonium sulfate over the temperature range 24 °C to -10 °C, shown as the solid squares in Figure 1. For comparison, the DRH's of ammonium sulfate particles measured by others as a function of temperature are shown in the figure as open symbols [*Braban et al.*, 2001; *Cziczo and Abbatt*, 1999; *Cziczo et al.*, 1997; *Onasch et al.*, 1999], and the DRH predicted from theory is shown as the solid line. [*Tabazadeh and Toon*, 1998]. For a complete description of the thermodynamics involved, see *Clegg et al.* [1998]. Within the experimental error, the DRH's we have measured from the bulk experiments agree well with the known values for ammonium sulfate. This confirms that a bulk study is an accurate way to determine the DRH of aerosols.

[14] The temperature dependent values for the DRH for the pure dicarboxylic acids are summarized in Table 3. While few previous measurements are available for the deliquescence of organics, our DRH measurements at 24 °C of pure

Table 2. Eutonic Composition Expressed as a Mole Fraction

	24 °C		4 °C		-10 °C	
	Organic	$(\text{NH}_4)_2\text{SO}_4$	Organic	$(\text{NH}_4)_2\text{SO}_4$	Organic	$(\text{NH}_4)_2\text{SO}_4$
Water Soluble Organics						
Malonic Acid	0.16	0.10	0.15	0.08	0.06	0.09
Glutaric Acid	0.08	0.07	0.01	0.09	0.01	0.08
Maleic Acid	0.11	0.09	0.07	0.08	0.07	0.07
L-Malic Acid	0.25	0.13	0.15	0.08	0.15	0.07
Less Soluble Organics						
Oxalic acid	0.006	0.095	0.003	0.090		
Succinic acid	0.004	0.094	0.002	0.086		
Adipic acid	0.005	0.096	0.001	0.087		

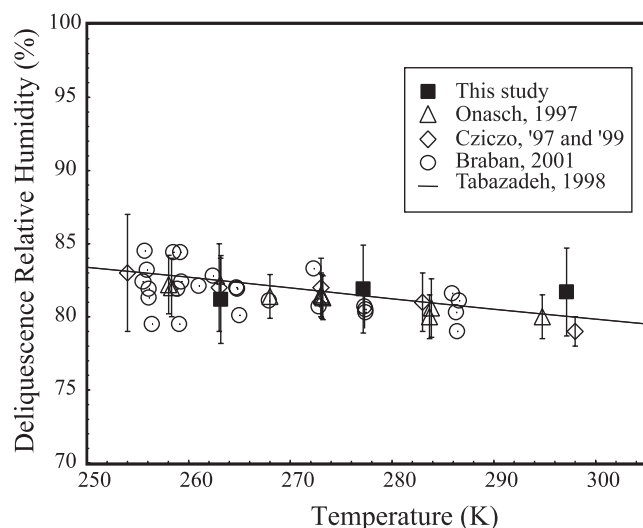


Figure 1. Comparison between our bulk determination of DRH and experimental aerosol and theoretical results from previous studies.

adipic acid and pure succinic acid, $\geq 95\%$ and $91 \pm 3\%$, respectively, are consistent with *Prezzi et al.*'s [2002] DRH results of $>93\%$ and $>92\%$, respectively. For the glutaric acid in water, our value of $87.5 \pm 3\%$ agrees within error to that reported by *Cruz and Pandis* [2000] of $85 \pm 5\%$. From Table 3, it can be seen that the DRH of each of the pure organics increases with decreasing temperature. Table 3 also shows the DRH of the eutonic mixtures as a function of temperature. For all of the soluble organics, the eutonic mixtures deliquesce at a lower RH than either of the pure solutions. In contrast, for the less soluble organics, the change in the DRH is smaller than the experimental error and could not be measured. For the eutonic mixtures, there was no uniform temperature trend for the DRH.

[15] The room temperature DRH of pure organics, pure ammonium sulfate and mixed soluble organic/ammonium sulfate for a range of compositions for each system containing a water-soluble organic are shown in Figure 2. The filled symbols indicate the eutonic composition for each system. The composition in units of organic molar ratio, defined as

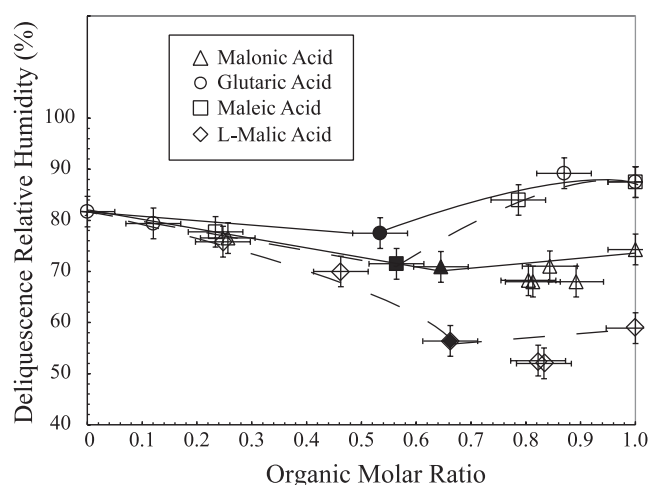


Figure 2. The RH measured over saturated solutions as a function of molar ratio at 24°C , where organic molar ratio is defined as moles of organic/(moles of organic plus moles of ammonium sulfate). Eutonic compositions are designated by filled-in symbols.

the moles of organic divided by the moles of organic plus the moles of ammonium sulfate, is shown on the x-axis. For malonic, maleic, and L-malic acids, the eutonic composition has a significantly lower DRH than either the pure ammonium sulfate or the pure organic. For the glutaric acid, the eutonic DRH is only slightly lower than the pure ammonium sulfate. This finding agrees within error with results from an earlier study by *Cruz and Pandis* [2000] who determined the DRH for 0.2, 0.5, and 0.8 molar ratio of glutaric acid with ammonium sulfate to be constant at $79 \pm 1\%$. While no direct comparison can be made since the molar ratios studied differ from those in our study, the measurements are likely to agree within error for the mixed glutaric acid/ammonium sulfate compositions. It is interesting to note that at low molar ratio organic, all the dicarboxylic acids behaved similarly, causing a decrease in the DRH compared to ammonium sulfate. In contrast, at higher organic molar ratio, the DRH varies with the identity of the organic as well as molar ratio organic. Here DRH's of the mixed systems are varied and reflect the wide range of the DRH's of the corresponding organic components in water.

[16] Our measurements of the RH over saturated solutions of the less water-soluble organics at 24°C and 4°C are also included in Table 3. For each organic, at each temperature, the mole fraction organic in the eutonic solutions is very low, 0.006 mole fraction or less. Thus the eutonic composition in each case contains mostly ammonium sulfate and water. In each of the less soluble cases, the eutonic composition has a DRH which is the same, within experimental error, as the DRH of the ammonium sulfate in water. We obtained the same result whether our organic/ammonium sulfate solution was prepared in eutonic proportions or with a large excess of the organic. In contrast, the DRH's of the less water-soluble organics in water are all much higher than the DRH's of pure ammonium sulfate and of the eutonic compositions. In each of the less soluble cases, a layer of organic on top of the eutonic solutions was visible to the naked eye. Once the solutions were filtered using a Buchner funnel with a coarse glass frit, the organic was no longer visible, indicating that it was excess solid organic.

Table 3. Deliquescence Relative Humidities (DRH)

	DRH		
	24°C	4°C	-10°C
Pure species in water			
Ammonium sulfate	81.7	81.9	81.2
Malonic Acid	74.3	80.6	88.5
Glutaric Acid	87.5	94.2	frozen
Maleic Acid	87.5	91.9	frozen
L-Malic Acid	58.9	66.0	frozen
Oxalic Acid	93.0	≥ 95.0	
Adipic Acid	≥ 95.0	≥ 95.0	
Succinic Acid	91.0	≥ 95.0	
Eutonic mixtures			
Malonic Acid /Ammonium Sulfate	70.9	71.7	77.4
Glutaric Acid /Ammonium Sulfate	77.5	74.1	79.8
Maleic Acid /Ammonium Sulfate	71.5	74.2	72.8
L-Malic Acid /Ammonium Sulfate	56.4	58.0	69.9
Oxalic Acid /Ammonium Sulfate	77.3	82.0	
Adipic Acid /Ammonium Sulfate	80.4	83.5	
Succinic Acid /Ammonium Sulfate	82.9	82.5	

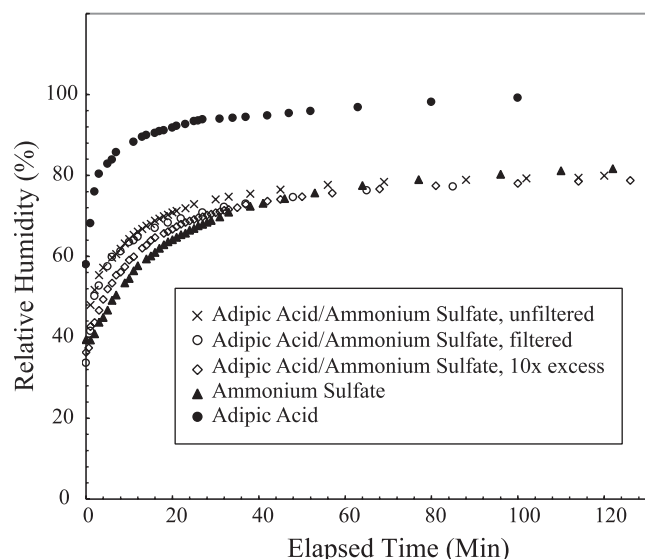


Figure 3. The RH of solutions as a function of time.

[17] To test whether the possible presence of organic at the surface could cause any kinetic hindrance to equilibration between the solution and the gas above it, we conducted a kinetic experiment on adipic acid, a less soluble compound in ammonium sulfate solution. Solutions of ammonium sulfate in water, adipic acid in water, adipic acid/ammonium sulfate in eutonic portions, and adipic acid/ammonium sulfate containing 10 times excess adipic acid were prepared in test tubes. A second adipic acid eutonic solution was prepared and filtered to remove any undissolved solids. The solutions were then exposed to prepurified nitrogen to lower the RH. Simultaneously the nitrogen was removed and the test tube was capped. Then the RH was monitored as the air in the test tube came to equilibrium with the solution. The time dependent RH results for the 5 samples are shown in Figure 3. It can be seen that within error, the RH as a function of time for the mixed systems, regardless of the method of preparation, is the same as the ammonium sulfate in water. While the adipic acid in water starts and ends at higher RH's, the shape of the curve is similar. As shown in the figure, in all cases, the systems were nearly equilibrated in sixty minutes. We conclude that any organic present on top of the adipic acid/ammonium sulfate solutions does not kinetically hinder equilibration between the solution and its surroundings.

4. Conclusions and Atmospheric Implications

[18] The solubilities of each of the organics we studied in aqueous solution decreases as the temperature decreases. The temperature dependence of the solubilities of organic solutions in aqueous solution is reflected in the temperature dependence of the DRH's, with higher DRH at lower temperatures. At -10°C the solutions of pure glutaric, maleic, and L-malic acid freeze, while solutions of malonic acid do not. While it is unlikely that many exist, pure organic aerosols in the troposphere could be frozen.

[19] The solubilities of several dicarboxylic acids in ammonium sulfate, including maleic, glutaric, malonic, and L-malic acids, are quite high. In contrast, oxalic, adipic,

and succinic acids have much lower solubilities in ammonium sulfate. The solubility of each of the organics we studied in ammonium sulfate decreases as the temperature decreases.

[20] In the case of the soluble dicarboxylic acids, adding organic molar fractions up to and including eutonic proportions lowers the DRH below that found for pure ammonium sulfate. Of the organics studied, the maximum effect was observed for the eutonic mixture of L-malic acid/ammonium sulfate where the deliquescence was observed at 56% RH at 24°C rather than the 80% RH observed for pure ammonium sulfate. This suggests that atmospheric aerosols may become liquid at lower relative humidities than calculations based on pure ammonium sulfate would predict. In contrast, the presence of the less soluble organics in solution has a minimal impact on the deliquescence RH of ammonium sulfate.

[21] **Acknowledgments.** The authors would like to thank Scot Martin for insightful discussions. This research was supported by the Biological and Environmental Research Program (BER), U.S. Department of Energy, under Grant No. DE-FG03-01ER63096.

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S. D. Brooks, M. E. Wise, M. Cushing, and M. A. Tolbert, Department of Chemistry & Biochemistry and CIRES, University of Colorado, Boulder 80309, USA.