Measurements of the Hygroscopic and Deliquescence Properties of Organic Compounds of Different Solubilities in Water and Their Relationship with Cloud Condensation Nuclei Activities

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The initial phase (solid or aqueous droplet) of aerosol particles prior to activation is among the critical factors in determining their cloud condensation nuclei (CCN) activity. Single-particle levitation in an electrodynamic balance (EDB) was used to measure the phase transitions and hygroscopic properties of aerosol particles of 11 organic compounds with different solubilities (10^{-1} to 10^2 g solute/100 g water). We use these data and other literature data to relate the CCN activity and hygroscopicity of organic compounds with different solubilities. The EDB data show that glyoxylic acid, 4-methylphthalic acid, monosaccharides (fructose and mannose), and disaccharides (maltose and lactose) did not crystallize and existed as metastable droplets at low relative humidity (RH). Hygroscopic data from this work and in the literature support earlier studies showing that the CCN activities of compounds with solubilities down to the order of 10^{-1} g solute/100 g water can be predicted by standard Köhler theory with the assumption of complete dissolution of the solute at activation. We also demonstrate the use of evaporation data (or efflorescence data), which provides information on the water contents of metastable solutions below the compound deliquescence RH that can be extrapolated to higher dilutions, to predict the CCN activity of organic particles, particularly for sparingly soluble organic compounds that do not deliquesce at RH achievable in the EDB and in the hygroscopic tandem differential mobility analyzer.

Introduction

Organic compounds contribute a substantial amount to the aerosol mass and play an important role in radiative forcing of atmospheric aerosols (*1*). Knowledge of the hygroscopicity of organic particles is essential in gaining a better understanding of the hygroscopicity and cloud condensation nuclei (CCN) activities of atmospheric particles. Recently, experimental and theoretical studies have examined the relationship between the hygroscopicity and CCN activity of laboratory-generated pure organic particles. Organic compounds in atmospheric particles have a wide range of solubilities in water (*2*). The activation of highly soluble organic compounds (e.g., malonic acid and glutaric acid (solubility > 100 g solute/100 g water)) can be predicted by the standard Köhler theory assuming complete dissolution of the solute at activation (*3, 4*). There are still uncertainties in predicting the CCN activity of sparingly soluble organic compounds that have solubilities on the order of 10^{-1} to 10^0 g solute/100 g water. The activation of some sparingly soluble organic compounds (e.g., aspartic acid, glutamic acid, homophthalic acid, and phthalic acid) agrees well with the predictions of standard Köhler theory, similar to more-soluble organic compounds (*5, 6*). On the other hand, the observed activation behavior of some sparingly soluble organic compounds (e.g., adipic acid and suberic acid) is not consistent with the predictions of standard Köhler theory. In addition to factors such as surface tension, wettability (*5*), aerosol generation method (*7*), aerosol morphology (*8*), curvature enhanced solubility (*9*), and impurities (*10*), the initial phase (solid or aqueous droplet) of single-component organic particles prior to activation has been taken into account in explaining the difference between modeled and experimental CCN data (*6, 8, 10*). Hori et al. (*8*) and Bilde and Svenningsson (*10*) have shown that metastable, highly concentrated aqueous–organic solution droplets had a much lower critical supersaturation than did dry solid particles of the same organic compounds. Hartz et al. (*6*) have observed that the existence of metastable solution droplets prior to activation can explain why some sparingly soluble organic compounds were highly CCN active, and why their critical supersaturations can be predicted by standard Köhler theory.

Laboratory hygroscopicity studies have shown that when the organic particles are initially formed as solution droplets, some sparingly soluble organic compounds can sustain a high level of supersaturation before crystallization occurs (*11, 12*). Furthermore, crystallization was not observed in some organic compounds with solubilities as low as less than 10^0 g solute/100 g water (*6*). Hence, the occurrence of crystallization of droplets containing organic compounds cannot be directly inferred from their solubility. Phase transitions and hygroscopic growth measurements of organic particles with different solubilities are needed for interpreting and predicting the hygroscopicity and CCN activity of organic particles.

In this study, we measure the hygroscopicity of 11 pure organic particles with different solubilities (10^{-1} to 10^2 g solute/100 g water) using single-particle levitation in an electrodynamic balance (EDB). These compounds were selected for their atmospheric relevance and available measured CCN activities. We report the hygroscopicity measurements and discuss how the phase transitions and hygroscopic growth of pure organic particles can be used to understand the organic particles' CCN behaviors at supersaturation and attempt to explain some of the differences between the modeled and experimental CCN data reported in the literature. We also compare the experimental data with predictions of the Universal Functional Group Activity Coefficients (UNIFAC) model, which has been used for estimating the water activity of different organic droplets (*13, 14*).

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Experimental Section

An EDB was used to levitate an aerosol particle of roughly 20–40 μm in diameter by electric fields. Hygroscopic measurements were performed by equilibrating the levitated particle of interest at different relative humidities for in situ relative mass determination. A detailed description is given in the Supporting Information (S2).

For saccharides and the compounds that crystallize, we assume that an anhydrous crystal is formed, and the data are presented in the form of the mass fraction of solute (mfs) as a function of relative humidity (RH) (*15, 16*). The uncertainties in this study were ±0.01 and ±0.03 in the mfs for the solution droplets and the solid particles, respectively. For the compounds that did not crystallize, the mass ratio, m/m_o in response to the RH change is reported, where m is the aerosol mass at a given RH and m_o is the aerosol mass at the reference RH (~6%RH). The uncertainties in this study were ±0.01 in m/m_o for the solution droplets and ±0.03 for the solid particles.

Results and Discussions

Deliquescent Organic Compounds. *C6–C9 Dicarboxylic Acids.* Dicarboxylic acids have been identified as a major group of water-soluble secondary organic compounds in atmospheric particles. Here, we report on hygroscopic measurements of adipic acid (C6), pimelic acid (C7), suberic acid (C8), and azelaic acid (C9) particles. The discussion on UNIFAC predictions is given in the Supporting Information (S3).

First, the EDB was equilibrated at 85%RH before introducing the particles. For solution droplets of adipic acid, suberic acid, and azelaic acid, they crystallized immediately when introduced into the EDB and formed solid particles. The levitated particles exhibited irregular light scattering, which did not resemble anything from the Mie scattering pattern of droplets. Furthermore, the balancing levitation voltage of the solid particles did not change with RH. Hence, these droplets have crystallization RH (CRH) larger than 85%RH. Once the solution droplets of adipic acid and azelaic acid crystallized, the solid particles did not deliquesce at RH < 90% (Figure 1a). Solid suberic acid particles were small because it has a low solubility (0.242 g/100 g water). The solubility lowers the initial size of the particles that can be trapped and levitated in the balance after equilibration even at a high RH (e.g., 85%RH). The size of the particles is so small that the particles cannot be levitated stationary in the balance. Our adipic acid measurements were consistent with those of Prenni et al. (*17*) and Hämeri et al. (*18*), who reported that there was no detectable increase in the size of solid adipic acid particles at RH < 93% using a hygroscopic tandem differential mobility analyzer (HTDMA). Corresponding to their low solubility, the water activities, $a_{w,sat}$ of saturated adipic acid, suberic acid, and azelaic acid solutions were determined to be 0.998, 0.999, and 0.999, respectively (Table 1). Solution droplets of pimelic acid crystallized at 51.5–53.0%RH, and the resulting solid pimelic acid particles did not deliquesce at RH < 90%. The absence of deliquescence of solid pimelic acid particles below 90%RH was consistent with the high deliquescence RH (DRH) value inferred from the measured $a_{w,sat}$ of the saturated pimelic acid solution (99.5%RH) (Table 1). Table 1 summarizes the hygroscopicity of the C2–C9 diacids determined in this work and in prior studies (*11, 19–21*). For the deliquescent compounds which crystallized in the EDB experiments but did not deliquesce at RH < 90%, such that the DRH cannot be observed directly, the measured a_w in bulk saturated solution experiments (see column in Table 1) was used for determining the DRH. There is no corresponding DRH or $a_{w,sat}$ for the nondeliquescent compounds which do not crystallize in EDB experiments.

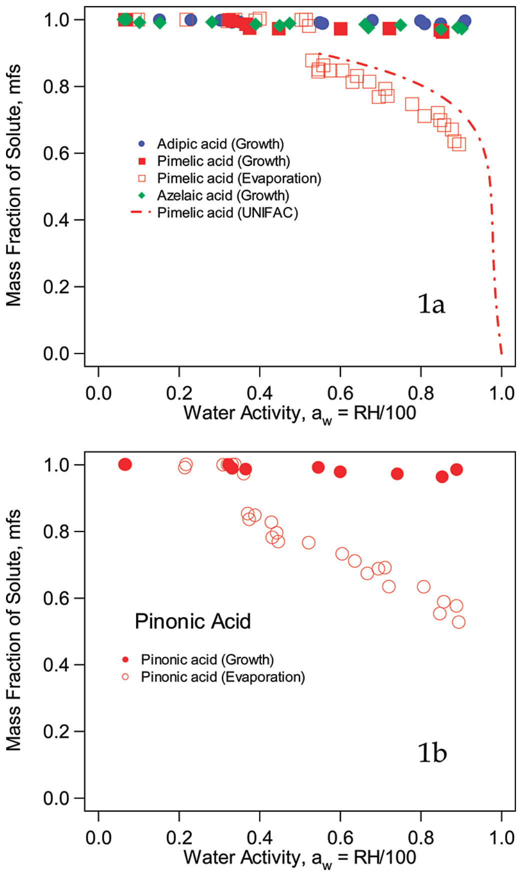

FIGURE 1. Deliquescent compounds: (a) the hygroscopicity of adipic acid, pimelic acid, and azelaic acid particles; (b) the hygroscopicity of *cis*-pinonic acid particles.

cis-Pinonic Acid. cis-Pinonic acid is a major product of the ozone oxidation of α-Pinene and is a major biogenic secondary compound. Figure 1b shows that the pinonic acid solution droplets crystallized to form solid particles at 33.9–37.1%RH. The solid pinonic acid particles did not deliquesce at RH < 90%. Cruz and Pandis (*20*) did not observe particle growth at RH less than 95% using HTDMA. The measured a_w of the saturated pinonic acid solution in this study was 0.999 (Table 1), which is in good agreement with the a_w of the pinonic acid solution with 0.5 wt% which was equal to 0.9993 (*22*). According to the solubility determined by Hartz et al. (*6*), the saturation concentration of pinonic acid solution is about 0.64–0.71 wt%.

Nondeliquescent Organic Compounds. *Monosaccharides (Fructose, Mannose) and Disaccharides (Maltose, Lactose).* Monosaccharides (e.g., glucose, fructose, and mannose) and disaccharides (e.g., maltose, lactose, and sucrose) have been detected in atmospheric particles originating from biomass burning (*23, 24*). We measured the hygroscopicity of two monosaccharides (fructose and mannose) (Figure 2a) and two disaccharides (maltose and lactose) (Figure 2b). The bulk solution data for fructose, maltose, and lactose were obtained from other studies (*25–27*).

As shown in Figure 2a,b, a smooth curve is observed for these four saccharides, suggesting that the aerosol particles absorbed and desorbed water reversibly and existed as liquid at RH as low as ~6%. These reversible water sorption and desorption characteristics without hysteresis were observed in other saccharides, such as glucose (*15*) and sucrose (*16*). Data on glucose particles from Peng et al. (*15*) were included for comparison (Figure 2a). There is no significant difference in the mfs–a_w curves of the different monosaccharides (Figure 2a). The disaccharides also exhibit very similar hygroscopicity

TABLE 1. Physical Properties and Hygroscopicity of Pure Organic Particles[a]

Deliquescent Compounds

dicarboxylic acids and others	purity (%)	molecular wt (g/mol)	solubility (g/100 g water)	crystal density (g/cm^3)	CRH (%RH)	DRH (%RH)	$a_{w,sat}$ (%RH)	κ^{b} (EDB)	κ^{c} (TDMA)	κ^{d} (CCN)
oxalic acid (C2)		90.04	12^{f}	1.90^{f}	$51.8–56.7^{f}$, $<5^{g}$, no ^{h}	$>90^{f}$, $96.8–98^{g}$	97.3^{f}, 97.1^{i}, 97.8^{j}	0.587 ± 0.061		
malonic acid (C3)		104.06	161^{f}	1.63^{f}	not obs.^{f}, 6 ± 3^{g}	not obs.^{f}, $69–91^{g}$	65.2^{f}, 71.9^{i}, 72.4^{j}	0.303 ± 0.029	0.44	0.227
succinic acid (C4)		118.09	8.8^{f}	1.552^{f}	$55.2–59.3^{f}$	$>90^{f}$	98.8^{f}, 97.6^{i}, 99.1^{j}	0.276 ± 0.026	<0.006	0.231
glutaric acid (C5)		132.12	116^{f}	1.429^{f}	$29–33^{f}$	$83–85^{f,k}$	88.5^{f}, 88.9^{i}, 88.2^{j}	0.176 ± 0.016	0.2	0.195
adipic acid (C6)	99	146.16	2.49^{l}	1.362^{l}	>85	not obs.^{m}	99.8, 99.9^{j}		<0.006	0.096
pimelic acid (C7)	99	160.17	6.73^{l}	1.321^{l}	51.5–53	not obs.^{m}	99.5	0.092 ± 0.009		
suberic acid (C8)	>98.0	174.20	0.242^{l}	1.272^{l}	>85	not obs.^{m}	99.9			
azelaic acid (C9)	98	188.22	0.5^{l}	1.251^{l}	>85	not obs.^{m}	99.9			0.018
cis-pinonic acid	98	184.23	$0.64–0.71^{l}$	0.781^{k}, 1.169^{l}	33.9–37.1	not obs.^{m}	99.9	0.224 ± 0.017	<0.006	0.106

Nondeliquescent Compounds

saccharides and others	purity (%)	molecular wt (g/mol)	solubility (g/100 g water)	crystal density (g/cm^3)	CRH (%RH)	DRH (%RH)	κ^{b} (EDB)	κ^{c} (TDMA)	κ^{d} (CCN)	κ^{e} (bulk soln)
glucose		180.2	90.9^{n}	1.566^{n}	N.A.^{o}	N.A.^{o}	0.185 ± 0.017		0.17	0.168
fructose	99	180.2	407.4^{n}	1.600^{n}	N.A.	N.A.	0.180 ± 0.017		0.17	0.171
mannose	>99.5	180.2	250^{n}	1.539^{n}	N.A.	N.A.	0.183 ± 0.017		0.17	0.170
maltose	>99	342.3	9.3^{n}	1.538^{n}	N.A.	N.A.	0.085 ± 0.008		0.093	0.091
lactose	>99.5	342.3	20^{n}	1.543^{n}	N.A.	N.A.	0.082 ± 0.008		0.093	
sucrose		342.3	200^{n}	1.589^{n}	N.A.^{p}	N.A.^{p}			0.093	
phthalic acid		166.10	0.41^{l}	1.593^{l}	N.A.^{l}	N.A.^{l}	0.059 ± 0.006	0.059	0.051	
homophthalic acid		178.11	0.46^{l}	1.41^{l}	N.A.^{l}	N.A.^{l}	0.081 ± 0.008	0.081	0.094	
4-methylphthalic acid	99	178.11	0.4^{l}	1.41^{l}	N.A.	N.A.	0.182 ± 0.017		0.147	
glyoxylic acid	>99.0	74.04	–	1.342	N.A.	N.A.	0.306 ± 0.029			

[a] N.A. refers to cases in which no crystallization was observed for the aerosol particles. [b] κ-values were derived from evaporation data at ~90%RH; dry particles were assumed for glyoxylic acid and 4-methylphthalic acid in the calculations. [c] κ-values were derived from growth data at ~90%RH and were obtained from Petters and Kreidenweis (*40*). [d] κ-values were derived from CCN data and were obtained from Petters and Kreidenweis (*40*). [e] κ-values were derived from bulk solution data at 95%RH obtained from Rosenørn et al. (*27*). [f] Peng et al. (*11*). [g] Braban et al. (*19*). [h] Prenni et al. (*17*). [i] Wise et al. (*21*). [j] Marcolli et al. (*41*). [k] Cruz and Pandis (*20*). [l] Hartz et al. (*6*). [m] Deliquescence was not observed for the solid particles at RH < 90% in this work. [n] Rosenørn et al. (*27*). [o] Peng et al. (*15*). [p] Choi and Chan (*16*).

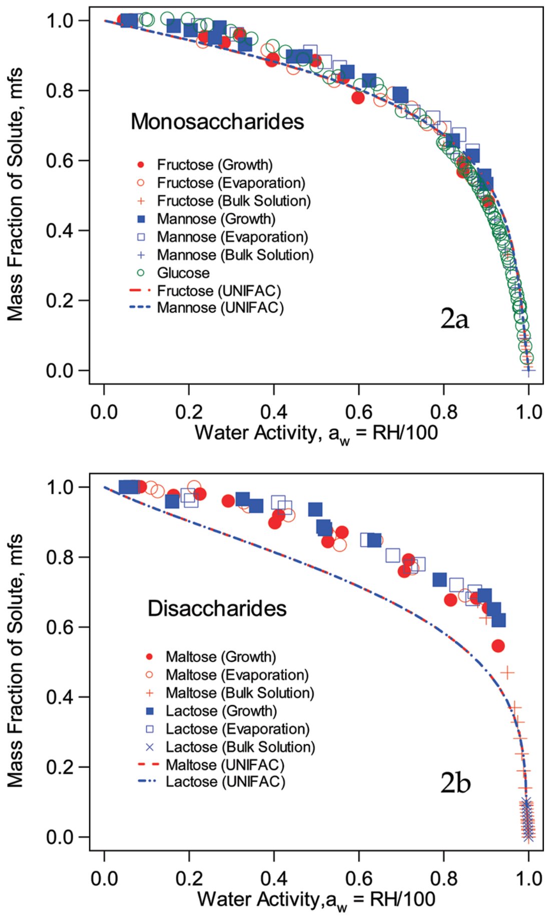

FIGURE 2. Nondeliquescent compounds: (a) the hygroscopicity of monosaccharides particles; (b) the hygroscopicity of disaccharides particles.

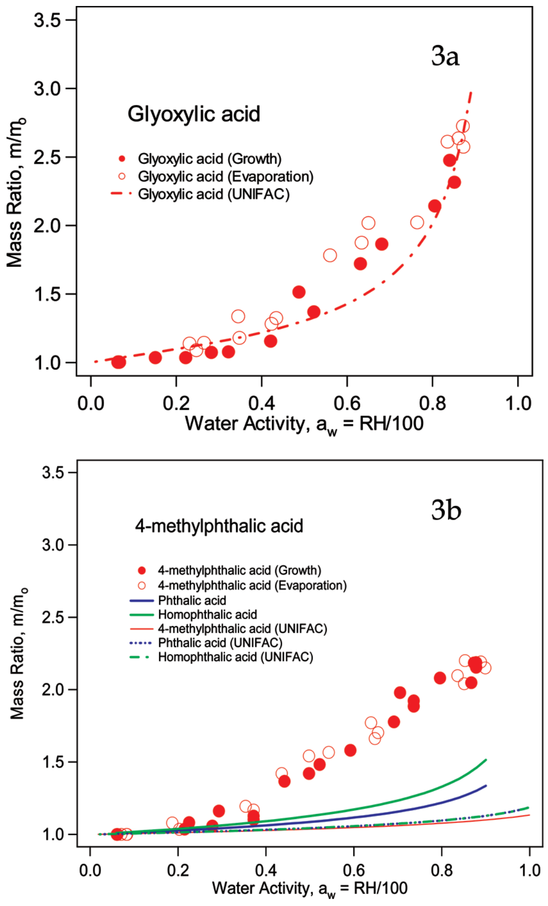

FIGURE 3. Nondeliquescent compounds: (a) the hygroscopicity of glyoxylic acid particles; (b) the hygroscopicity of 4-methylphthalic acid particles.

(Figure 2b). The monosaccharides were slightly more hygroscopic than the disaccharides were at high RH. Our findings are in agreement with those of Rosenørn et al. (*27*), who found that a group of monosaccharides (glucose, fructose, and mannose) were activated at almost the identical supersaturation, as were a group of disaccharides (sucrose, lactose, and maltose) in their CCN measurements. It is not surprising that very similar hygroscopicity and CCN activity were observed for these saccharides, which have very similar chemical structures within the same group. It is also noted that these four saccharide particles started to uptake a small amount of water at relatively low RH. We summarize the hygroscopicity of the mono- and disaccharide particles in Table 1. Crystallization has not been observed for other biomass burning derived saccharides, such as levoglucosan, mannosan, and galactosan (*12, 28, 29*). The presence of these organic compounds reinforces field measurements that biomass burning particles (or smoke particles) uptake water at relatively low RH (*30*).

Glyoxylic Acid. Modeling and laboratory studies suggest that aqueous phase reactions of water-soluble organics (e.g., pyruvic acid, glyoxal, methylglyoxal, and glycolaldehyde) can yield secondary organic aerosols through the formation of carboxylic acids (e.g., glyoxylic acid, glycolic acid, and oxalic acid) (*31–33*). As shown in Figure 3a, there is an absence of the stepwise increase or decrease in the mass ratio, suggesting that glyoxylic acid particles existed as metastable solution droplets at RH as low as 6%RH. At the lowest RH, the m/m_o value equal to unity does not necessarily suggest that the glyoxylic acid particles were anhydrous. Glyoxylic acid has a polar functional group (carboxylic acid) and likely retains water at low RH. If m_o were defined as the water-free particle mass, the reported m/m_o value under that definition would be larger than the one we report here.

4-Methylphthalic Acid. Like homophthalic acid and phthalic acid (*6*), 4-methylphthalic particles may retain some water at low RH, as shown in Figure 3b. The $m/m_o - a_w$ curves of homophthalic acid and phthalic acid particles are included in the figure for comparison. The diameter growth factors, G_f, of homophthalic acid and phthalic acid particles have been reported by Hartz et al. (*6*). The G_f, and m/m_o values can be interchanged using $G_f = [(\rho_s/\rho_w)(m/m_o - 1) + 1]^{1/3}$ where ρ_s and ρ_w are the density of the organic crystals and water, respectively. This equation is also used in the κ-water activity equation, which is based on the volumes of water and solute in the particle, not mass (as discussed later).

All three sparingly soluble organic acids remained as solution droplets and experienced small growth at relatively low RH. Among these three acids, 4-methylphthalic acid was the most hygroscopic, followed by homophthalic acid and phthalic acid. Compared with homophthalic acid (52 ± 12nm) and phthalic acid (63 ± 18nm), 4-methylphthalic acid had the lowest activation diameter (45 ± 8 nm) and was the most CCN active, as observed by Hartz et al. (*6*) at 1% supersaturation.

Relationship between Initial Aerosol Phase and CCN Activity. Recent laboratory CCN experiments have shown that the activation of highly soluble organic compounds (solubility larger than ~100 g solute/100 g water, e.g., malonic acid and glutaric acids) can be predicted by standard Köhler theory (*3, 4*). However, there are still uncertainties in predicting the activation of sparingly soluble organic compounds using standard Köhler theory. Hartz et al. (*6*) have reported that the CCN activities of organic compounds with solubilities as low as 10^{-1} g solute/100 g water (e.g., aspartic acid, glutamic acid, homophthalic acid, and phthalic acid) were in good agreement with the predictions from standard Köhler theory using the assumption that all solutes were completely dissolved in the droplets at activation. This may be explained by noting that these aerosol particles did not crystallize and likely remained as metastable solution droplets after the diffusion dryer in the laboratory CCN measurements (*6*). This hypothesis also suggests that standard Köhler theory is valid for other organic compounds that do not crystallize at very low RH, irrespective of their solubility. Our hygroscopicity data (Figure 3b), which showed water uptake at all RHs studied, support the use of standard Köhler theory for sparingly soluble 4-methylphthalic acid, as suggested by Hartz et al. (*6*). It is noted that the complete solute dissolution behavior at activation observed in Hartz et al.'s (*6*) study may also be related to other effects such as impurities, morphology, or surface tension depression (*8, 10*).

For some sparingly soluble organic compounds, solid particles were formed after the particles were passed through the diffusion dryer in CCN experiments. Hori et al. (*8*), Bilde and Svenningsson (*10*), and Kreidenweis et al. (*35*) have shown that dry submicrometer particles of sparingly soluble organic compounds are expected to deliquesce only under supersaturated conditions. In the absence of impurities in the particles, the critical supersaturation required for these pure dry submicrometer particles to activate can be predicted by the larger of two supersaturations: that required for deliquescence of pure dry solid particles or that predicted from standard Köhler theory assuming the complete dissolution of solute at activation (*8, 10, 35*). Kreidenweis et al. (*35*) have suggested that deliquescence-controlled activation may likely occur for organic compounds which have saturated a_w ($a_{w,sat}$) values larger than 0.97, corresponding approximately to solubilities smaller than 10–40 g solute/100 g water. These solubility and $a_{w,sat}$ ranges should be considered as a reference, rather than as strict threshold values at which these activation phenomena occur.

The activation of some dry solid sparingly soluble organic particles (e.g., succinic, pimelic, azelaic, and *cis*-pinonic acids) was found to agree more closely with that predicted by standard Köhler theory with complete solute dissolution, although the agreement was barely within the error limits (*6*). This observed enhancement in the CCN activity, over that expected if deliquescence activation were controlling, may be attributed to the impurities which come from the chemicals or solvents used for aerosol generation (e.g., water). Bilde and Svenningsson (*10*) have shown that a small amount (~2 wt%) of NaCl is sufficient to reduce the critical supersaturation of dry 80 nm succinic acid particles to that predicted by standard Köhler theory. An even smaller percentage of NaCl is needed to show similar effects for larger particles. It appears that the activation of such particles is dominated by the highly soluble impurity that begins to add water to the particle at relatively low RH, initiating some dissolution of the organic compound. It is not unreasonable to assume that the effect of impurities on CCN activation of single-component organic particles that are classified as "sparingly soluble" is significant in previous CCN measurements, unless otherwise stated.

For each pure dry organic sparingly soluble compound, there is a minimum dry diameter, D_{min} (and corresponding critical supersaturation) for which the dry particle is completely dissolved at activation. For larger dry diameters ($D > D_{min}$), the activation behavior obeys standard Köhler theory because the DRH is always lower than the maximum saturation in the Köhler curve. For smaller dry diameters ($D < D_{min}$), the activation behavior should be limited by deliquescence, and observations should demonstrate a very strong sensitivity of critical supersaturation to particle size (*8*). When $D = D_{min}$, $S_{deliquesence} = S_{Köhler}$. It can be difficult to estimate precisely where this transition occurs because saturation water activities are not generally known with great precision and because the transition point is highly sensitive to the presence of even very trace amounts of soluble impurities. Particle morphology may also play a role in changing the transition points from that expected for a spherical, dry particle (*8*).

For laboratory-generated organic particles, factors such as impurities, surface tension, and morphology should be considered when analyzing the CCN data (*6, 8, 10*). Impurities in dry organic particles may be ubiquitous (*10*) and may lower the deliquescence-controlled activation to the extent that the organic particles activate according to standard Köhler theory. The effect of impurities on the CCN activity of sparingly soluble organic particles needs to be addressed in future measurements. Some single-component organic particles may be only partially dried after passing through the dryer in CCN measurements and before activation, due to incomplete drying processes or the presence of impurities that retain water to low RH (e.g., NaCl). The effects of these factors may lower the deliquescence point and thus critical supersaturation. This may help explain why some dry sparingly soluble organic compounds activate at conditions between the standard Köhler theory prediction and the DRH of pure dry organic particles. Modified Köhler theory, which accounts for the presence of multiple components and the gradual dissolution of solute in a growing droplet, may be used to predict the activation of these organic particles.

Figure 4 summarizes how the initial aerosol phase affects the prediction of the CCN activity of particles composed of pure organic compounds with different solubilities and hygroscopicities. This discussion is only relevant for interpretation of pure dry single-component particles in laboratory CCN experiments. For those compounds which do not crystallize (nondeliquescent), the complete dissolution of the solute at activation can always be assumed. For those compounds which crystallize (deliquescent compounds), the initial phase may play a role in the CCN activity and the observations of the effect of the initial phase on the CCN behaviors reported in the literature also depend on impurities and particle size. It is noted that if solute dissolution or deliquescence kinetics is significant in the time scale of the experiments, kinetic limitations on the aerosol hygroscopicity and cloud formation may also need to be considered (*36*). For soluble organic compounds ($a_{w,sat} < 0.97$), deliquescence always occurs under subsaturated conditions (RH < 100%), and the solutes are completely dissolved before activation. The activation can always be predicted by standard Köhler theory, irrespective of the initial aerosol phase.

Relationship between Hygroscopic Growth and CCN Activity. The hygroscopicity and CCN activity of selected organic particles have been measured by a number of researchers (*29, 37, 38*). The activation of organic particles can be modeled using Köhler theory based on the measurements of their hygroscopic growth data. Koehler et al. (*39*) have shown that the critical dry diameters for oxalic acid, glutaric acid, malonic acid, levoglucosan, glucose, and fructose at supersaturations between 0.2 and 1% can be estimated from hygroscopic growth data from HTDMA or EDB experiments within experimental error (±20%). Petters and Kreidenweis (*40*) introduced a single hygroscopicity parameter, κ, to describe the hygroscopicity and CCN activity of organic aerosol particles under both subsaturation (RH < 100%) and supersaturation (RH > 100%):

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad (1)$$

where a_w is the water activity, V_s is the volume of the dry particle and V_w is the volume of water. The κ-values are calculated using the EDB evaporation data to estimate the

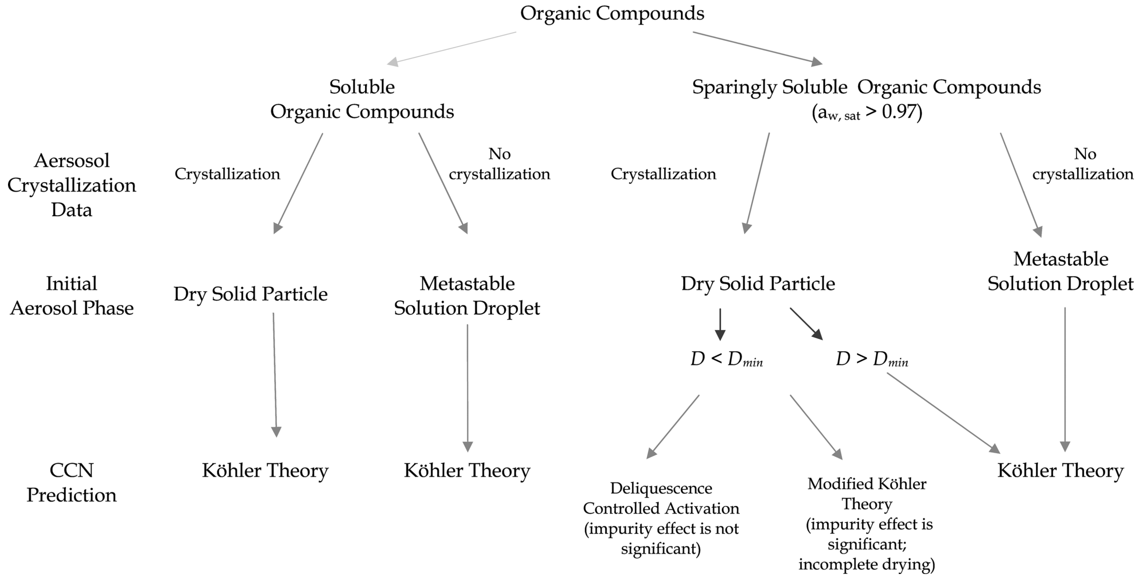

FIGURE 4. Role of initial aerosol phase prior activation on the prediction of the CCN activity of organic compounds with different solubilities and hygroscopicities. Particle diameter is denoted as D, and D_{min} is the smallest diameter for which the particle is completely dissolved at activation (see text). When $D = D_{min}$, $S_{deliquscence} = S_{Köhler}$.

ratio of the volume of the dry particle to that of water at a given RH (or a_w). We estimated the particle density, ρ_p, using volume additivity:

$$\frac{1}{\rho_p} = \frac{\mathrm{mfs_w}}{\rho_w} + \frac{\mathrm{mfs_s}}{\rho_s}$$

where $\mathrm{mfs_s}$ and $\mathrm{mfs_w}$ are the mass fraction of solute and water, and ρ_s and ρ_w are the densities of the solute and water, respectively. We have evaluated the uncertainty in the κ-value due to the particle density and mfs. The uncertainties of the κ-values are given in Table 1. We chose to evaluate the κ-value at ~90%RH in order to compare our results with other values reported in the literature. This is usually the largest RH for reliable HTDMA data, and the κ-values are evaluated at the most dilute conditions possible to better extrapolate to dilute conditions at CCN activity (*40*).

For organic compounds that deliquesced in the growth (or deliquescence) experiments or did not crystallize at low RH, Petters and Kreidenweis (*40*) found that the κ-value derived from the hygroscopic growth data at RH~90% can be used to predict the CCN activity, and the predictions are consistent with the κ-value derived from the measured CCN data. On the other hand, they found that no water uptake was observed for adipic acid or succinic acid at RH < 90% because of the very high DRH of these compounds (Table 1). The mean κ-values derived from the measured CCN data (0.231 for succinic acid and 0.096 for adipic acid) and the hygroscopic growth data (<0.006 for succinic and adipic acid) were thus not in agreement. High RH hygroscopicity measurements are needed to measure the deliquescence and hygroscopic growth of sparingly soluble organic compounds having high DRH. Dinar et al. (*37*) and Wex et al. (*38*) have addressed the necessity and experimental difficulties of hygroscopicity measurement at high RH to predict the CCN activity of aerosol particles based on hygroscopicity data.

One commonly used approach for estimating activation properties is to use the measured surface tension and water activity obtained from bulk solution measurements (*4*). However, the bulk water activity data are not always available, especially for compounds that have low solubility and crystallize easily in bulk solution studies. To date, there are relatively few hygroscopic measurements performed at RH > 95%, and the required RH range would be even higher for some sparingly soluble compounds. An alternative is to use, instead of hygroscopic growth (or "deliquescence") data, the evaporation (or "efflorescence") data obtained for levitated droplets, which can be supersaturated in EDB or HTDMA experiments and thus represent metastable solutions. On the basis of the approach proposed by Petters and Kreidenweis (*40*), we computed the κ-value at 90% RH using the evaporation data for succinic acid in EDB experiments determined by Peng et al. (*11*) to be 0.276, which is close to the mean κ-value derived from the experimental CCN data (0.231) and is larger than the κ-value implied by the growth data (<0.006). Inconsistency has also been observed in κ-values derived from hygroscopic growth data (<0.006) and CCN experimental data (0.063–0.196) for pinonic acid as reported by Petters and Kreidenweis (*40*). The κ-value derived from the evaporation data for pinonic acid (Figure 1b) is 0.224, which is slightly larger than the upper limit of the κ-value derived from the experimental CCN data (0.196). The κ-values of other organic compounds derived from the evaporation data at ~90%RH are also given in Table 1 and are in good agreement, within the experimental uncertainty, with the CCN-derived κ-values, assuming water surface tension at activation. For the nondeliquescent compounds, the evaporation and growth data are the same over the RH range studied, and the κ-values derived from evaporation and growth data are thus also the same. These results suggest that the evaporation (or efflorescence) data in the EDB or HTDMA experiments, particularly for sparingly soluble organic compounds, can be used to predict the CCN activity of aerosol particles. One should note that, since CCN activation generally occurs at conditions where the solutions are dilute, the κ-value calculated at the highest available %RH is most relevant. The κ-value is sensitive to the RH at which the data are chosen for calculation (*40*).

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Supporting Information Available

Details of the experimental procedures and bulk water activity measurement are given. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Kanakidou, M.; et al. Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.* **2004**, *4*, 5855–6024.

(2) Saxena, P.; Hildemann, L. M. Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. *J. Atmos. Chem.* **1996**, *24*, 57–109.

(3) Kumar, P. P.; Broekhuizen, K.; Abbatt, J. P. D. Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species. *Atmos. Chem. Phys.* **2003**, *3*, 509–520.

(4) Sun, J.; Ariya, P. A. Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review. *Atmos. Environ.* **2006**, *40*, 795–820.

(5) Raymond, T. M.; Pandis, S. N. Cloud activation of single-component organic aerosol particles. *J. Geophys. Res.* **2002**, *107*, 4787; doi:10.1029/2002JD002159.

(6) Hartz, K. E. H.; Tischuk, J. E.; Chan, M. N.; Chan, C. K.; Donahue, N. M.; Pandis, S. N. Cloud condensation nuclei activation of limited solubility organic aerosol. *Atmos. Environ.* **2006**, *40*, 605–617.

(7) Rissman, T. A.; Varutbangkul, V.; Surratt, J. D.; Topping, D. O.; McFiggans, G.; Flagan, R. C.; Seinfeld, J. H. Cloud condensation nucleus (CCN) behavior of organic aerosol particles generated by atomization of water and methanol solutions. *Atmos. Chem. Phys.* **2007**, *7*, 2949–2971.

(8) Hori, M.; Ohta, S.; Murao, N.; Yamagata, S. Activation capability of water soluble organic substances as CCN. *J. Aerosol Sci.* **2003**, *34*, 419–448.

(9) Padro, L. T.; Nenes, A. Cloud droplet activation: Solubility revised. *Atmos. Chem. Phys. Discuss.* **2007**, *7*, 2325–2355.

(10) Bilde, M.; Svenningsson, B. CCN activation of slightly soluble organics: the importance of small amounts of inorganic salt and particle phase. *Tellus, Ser. B* **2004**, *56*, 128–134.

(11) Peng, C. G.; Chan, M. N.; Chan, C. K. The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions. *Environ. Sci. Technol.* **2001**, *35*, 4495–4501.

(12) Chan, M. N.; Choi, M. Y.; Ng, N. L.; Chan, C. K. Hygroscopicity of water-soluble organic compounds in atmospheric aerosols: Amino acid and biomass burning derived organic species. *Environ. Sci. Technol.* **2005**, *39*, 1555–1562.

(13) Saxena, P.; Hildemann, L. M. Water absorption by organics: Survey of laboratory evidence and evaluation of UNIFAC for estimating water activity. *Environ. Sci. Technol.* **1997**, *31*, 3318–3324.

(14) Marcolli, C.; Peter, T. Water activity in polyol/water systems: new UNIFAC parameterization. *Atmos. Chem. Phys.* **2005**, *5*, 1545–1555.

(15) Peng, C. G.; Chow, A. H. L.; Chan, C. K. Hygroscopic study of glucose, citric acid, and sorbitol using an electrodynamic balance: comparison with UNIFAC predictions. *Aerosol Sci. Technol.* **2001**, *35*, 753–758.

(16) Choi, M. Y.; Chan, C. K.; Zhang, Y. H. Application of fluorescence spectroscopy to study the state of water in aerosols. *J. Phys. Chem. A* **2004**, *108*, 1133–1138.

(17) Prenni, A. J.; DeMott, P. J.; Kreidenweis, S. M.; Eli Sherman, D.; Russell, L. M.; Ming, Y. The effects of low molecular weight dicarboxylic acids on cloud formation. *J. Phys. Chem. A* **2001**, *105*, 11240–11248.

(18) Hämeri, K.; Charlson, R.; Hansson, H.-C. Hygroscopic growth of mixed ammonium sulfate and carboxylic acids particles. *AIChE* **2002**, *48*, 1309–1316.

(19) Braban, G. F.; Carroll, M. F.; Styler, S. A.; Abbatt, J. P. D. Phase transitions of malonic and oxalic acid aerosols. *J. Phys. Chem. A* **2003**, *107*, 6594–6602.

(20) Cruz, C. N.; Pandis, S. N. Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol. *Environ. Sci. Technol.* **2000**, *34*, 4313–4319.

(21) Wise, M. E.; Surratt, J. D.; Curtis, D. B.; Shilling, J. E.; Tolbert, M. A. Hygroscopic growth of ammonium sulfate/dicarboxylic acids. *J. Geophys. Res.* **2003**, *108*, 4638; doi:10.1029/2003JD003775.

(22) Varga, Z.; Kiss, G.; Hansson, H.-C. Modelling the cloud condensation nucleus activity of organic acids. *Atmos. Chem. Phys. Discuss.* **2007**, *7*, 5341–5364.

(23) Nolte, C. G.; Schauer, J. J.; Cass, G. R.; Simoneit, B. R. T. Highly polar organic compounds present in wood smoke and in the ambient atmosphere. *Environ. Sci. Technol.* **2001**, *35*, 1912–1919.

(24) Carvalho, A.; Pio, C.; Santos, C. Water-soluble hydroxylated organic compounds in German and Finnish aerosols. *Atmos. Environ.* **2003**, *37*, 1775–1783.

(25) Velezmoro, C. E.; Oliveira, A. L.; Cabral, F. A.; Antonio, J. A.; Meirelles, A. J. A. Prediction of water activity in sugar solutions using models of group contribution and equation of state. *J. Chem. Eng. Jpn.* **2000**, *33*, 645–653.

(26) Gaida, L. B.; Gros, D. J. B. Variable hydration of small carbohydrates for predicting equilibrium properties in diluted and concentrated solutions. *Food Chem.* **2006**, *96*, 387–401.

(27) Rosenørn, T.; Kiss, G.; Bilde, M. Cloud droplet activation of saccharides and levoglucosan particles. *Atmos. Environ.* **2006**, *40*, 1794–1802.

(28) Mochida, M.; Kawamura, K. Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles. *J. Geophys. Res.* **2004**, *109*, D212002; doi:10.1029/2004JD004962.

(29) Svenningsson, B.; Rissler, J.; Swietlicki, E.; Mircea, M.; Bilde, M.; Facchini, M. C.; Decesari, S.; Fuzzi, S.; Zhou, J.; Monster, J.; Rosenorn, T. Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance. *Atmos. Chem. Phys.* **2006**, *6*, 1937–1952.

(30) Kotchenruther, L.; Hobbs, P. V. Humidification factors from biomass burning in Brazil. *J. Geophys. Res.* **1998**, *103*, 32081–32089.

(31) Ervens, B.; Feingold, G.; Frost, G. J.; Kreidenweis, S. M. A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production. *J. Geophys. Res.* **2004**, *109*, D15205; doi:10.1029/2003JD004387.

(32) Lim, H.-J.; Carlton, A. G.; Turpin, B. J. Isoprene forms secondary organic aerosol through cloud processing: Model simulations. *Environ. Sci. Technol.* **2005**, *39*, 4441–4446.

(33) Carlton, A. G.; Turpin, B. J.; Lim, H.-J.; Altieri, K. E.; Seitzinger, S. Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds. *Geophys. Res. Lett.* **2006**, *33*, L06822; doi:10.1029/2005GL025374.

(34) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987; pp 324–330.

(35) Kreidenweis, S. M.; Petters, M. D.; DeMott, P. J. Deliquescence-controlled activation of organic aerosols. *Geophys. Res. Lett.* **2006**, *33*, L06801; doi:10.1029/2005GL024863.

(36) Chan, M. N.; Chan, C. K. Mass transfer effects in the hygroscopic measurement of aerosol particles. *Atmos. Chem. Phys.* **2005**, *5*, 2703–2712.

(37) Dinar, E.; Taraniuk, I.; Graber, E. R.; Anttila, T.; Mentel, T. F.; Rudich, Y. Hygroscopic growth of atmospheric and model humic-like substances. *J. Geophys. Res.* **2007**, *112*, D05211; doi:10.1029/2006JD007442.

(38) Wex, H.; Hennig, T.; Salama, I.; Ocskay, R.; Kiselev, A.; Henning, S.; Massling, A.; Wiedensohler, A.; Stratmann, F. Hygroscopic growth and measured and modeled critical supersaturations of an atmospheric HULIS sample. *Geophys. Res. Lett.* **2007**, *34*, L02818; doi:10.1029/2006GL028260.

(39) Koehler, K. A.; Kreidenweis, S. M.; DeMott, P. J.; Prenni, A. J.; Carrico, C. M.; Ervens, B.; Feingold, G. Water activity and activation diameters from hygroscopicity data - Part II: Application to organic species. *Atmos. Chem. Phys.* **2006**, *6*, 795–809.

(40) Petters, M. D.; Kreidenweis, S. M. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. *Atmos. Chem. Phys.* **2007**, *7*, 1961–1971.

(41) Marcolli, C.; Luo, B. P.; Peter. The mixing of the organic aerosol fractions: liquids as the thermodynamically stable phases. *J. Phys. Chem. A* **2004**, *108*, 2216–2224.

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