Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Supplemental Information:

Hygroscopicity of Polycatechol and Polyguaiacol Secondary Organic Aerosol in Sub- and Supersaturated Water Vapor Environments

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Summary: This supplemental document includes details on particle charging and SMCA, the method for determining the relative humidity within the H-TDMA setup using ammonium sulfate as a standard, the CCNC supersaturation calibration data, and the derivations of equations for the Brunauer-Emmett-Teller (BET) adsorption theory and Frenkel-Halsey-Hill (FHH) adsorption theory.

Details on the CCNC - Supersaturated Measurements and Particle Charging

Scanning mobility CCN analysis (SMCA) was used to calculate the activation diameter at each supersaturation.[1] SMCA addresses doubly-charged and triply-charged particles by placing them in their actual size bins using expression from Wiedensohler (1988).[2]

For particles with $n = +1, +2$ charges, charge corrections were computed using the following:

$$f(D_d, n) = 10^{\left(\sum_{i=0}^{5} a_i(n)\left(logD_d\right)^i\right)} \tag{S.1}$$

While for $n = +3$

$$f(D_d, +3) = \phi exp\frac{-\left(n - \frac{2\pi\varepsilon_o D_d kT}{e^2}\ln\left(\frac{Z_{i+}}{Z_{i-}}\right)\right)}{4\pi\varepsilon_o D_d kT/e^2} \tag{S.2}$$

where n is the number of charges, $a_i(n)$ are empirical coefficients presented in Wiedensohler (1988),[2] $\phi = e/\sqrt{4\pi^2\varepsilon_o D_d kT}$, e is the elementary charge, ε_o is the dielectric constant of air, k is the Boltzmann constant, T is absolute temperature, and $Z_{i+}/Z_{i-} = 0.875$ is the ion mobility ratio.

H-TDMA Growth Factor Calibration

Using ammonium sulfate as a standard, the H-TDMA calibration was done using Köhler Theory as described by **Equation (4)** found in the manuscript. Using the experimental growth factor of ammonium sulfate, which is calculated by dividing the geometric mean particle diameter by the selected dry particle diameter (**Figure S1**), the RH within the H-TDMA setup was determined from Taylor et al (2011).

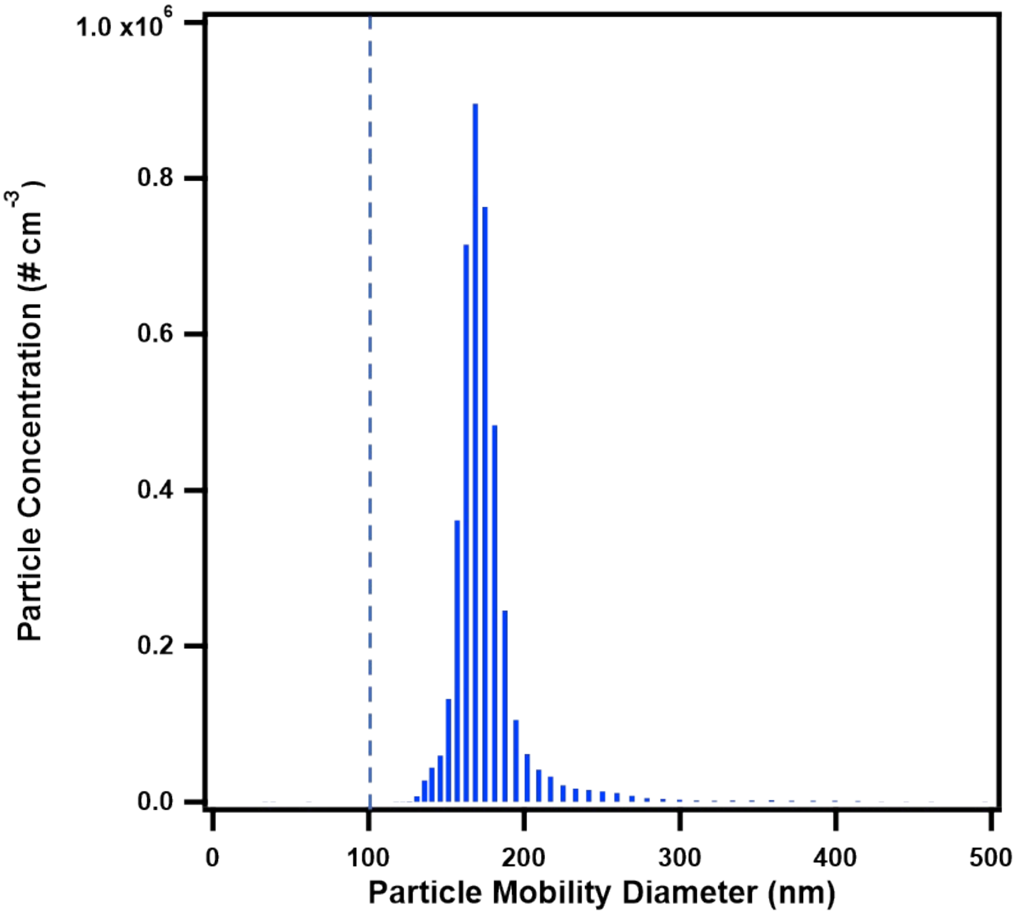

Figure S1. Example of ammonium sulfate direct growth factor determination (sheath flow = 3.0 lpm; aerosol flow = 0.3 lpm). Straight dotted line represents selected dry particle diameter while SMPS data represents aerosols post humidification.

CCNC Supersaturation Calibration

Table S1. $(NH_4)_2SO_4$ CCN Counter Calibration Data

Supersaturation Setting (%)	Calibrated Supersaturation (%)	Critical Diameter (nm)
0.4	0.47 ± 0.01	46.9 ± 0.6
0.6	0.63 ± 0.01	36.8 ± 0.4
0.8	0.81 ± 0.01	31.6 ± 0.3
1.0	1.07 ± 0.02	26.9 ± 0.3

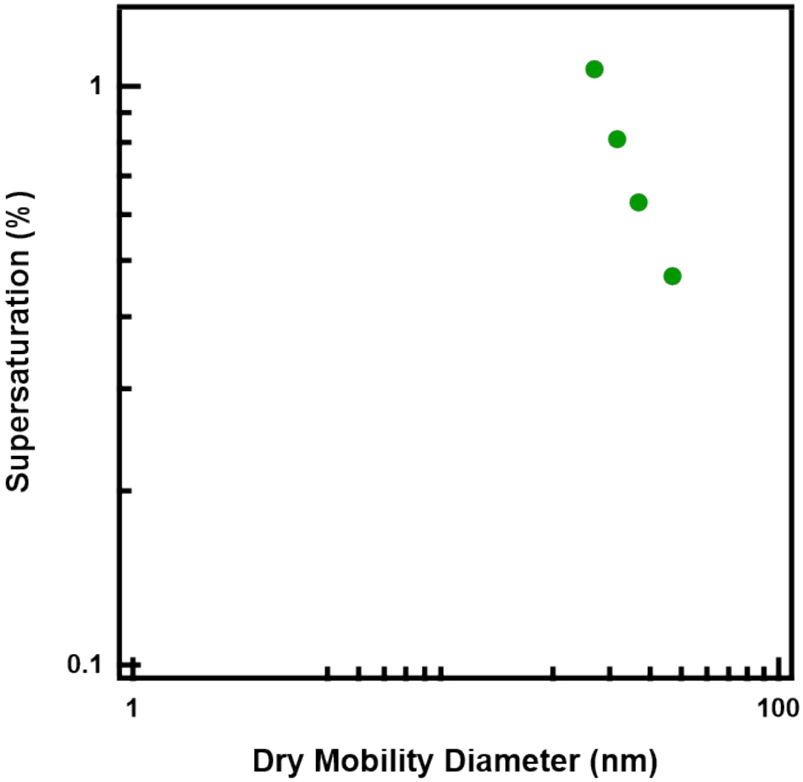

Figure S2. CCN counter supersaturation calibration using ammonium sulfate. The dry mobility diameter for each of the four different instrument supersaturation are provided.

Analysis and Calculations

Brunauer-Emmett-Teller (BET) Adsorption Theory

The Brunauer-Emmett-Teller (BET) theory provides an adsorption isotherm and is fundamentally a multilayer adsorption theory that can model physical adsorption of gases (such as water vapor) on solid particles.[3,4] BET is the first model to give good agreement with experimental data for vapor-on-solid adsorption. In context of droplet formation, BET explains the formation of aqueous multilayers on the dry aerosol particles suspended in the atmosphere. The typical formulation of the BET multilayer model is given as,

$$\Theta = \left(\frac{1}{1 - a_w}\right) \cdot \left(\frac{c \cdot a_w}{1 - a_w + c \cdot a_w}\right) \tag{S.3}$$

where Θ is the thickness of water adsorbed on the surface of the dry particle (also known as the surface coverage), c is the temperature-dependent model fit parameter, and a_w is the water activity coefficient, which is equivalent to the relative humidity over the aerosol particle, defined as the ratio of the ambient vapor pressure and saturation vapor pressure at the given temperature (T). If the total and monolayer volume of the adsorbed water in the droplet are denoted by V and V_m respectively, the surface coverage can be defined as (Tang et al., 2016),

$$\Theta = \frac{V}{V_m} = \frac{\frac{\pi}{6}\left(D_{wet}^3 - D_{dry}^3\right)}{\pi D_{dry}^2 D_w} = \frac{D_{wet}^3 - D_{dry}^3}{6 D_{dry}^2 D_w} \tag{S.4}$$

where D_{dry}, D_{wet} and $D_w = 2.75\text{Å}$ are the diameters of the dry particle, droplet, and water molecule, respectively. If the thickness of the adsorbed layer is small, then Equation (S.4) can be approximated as $\Theta = \frac{D_{wet} - D_{dry}}{2 \cdot D_w}$ instead. The constant c is a Boltzmann term which is basically related to 2 types of adsorption energies in a droplet growth system – the adsorption energy for a water molecule on the particle surface, and the energy of adsorption onto the existing water multilayer.[3] More intuitively, it is assumed that c is related to the free energies of the system and is given as,

$$c = \exp\left(\frac{-\Delta G}{RT}\right) \tag{S.5}$$

where ΔG is related to the 2 adsorption energies mentioned above and is mathematically given as ($\Delta G_{ads} - \Delta G_{vap}$) where ΔG_{ads} is the surface adsorption free energy change of the particle-water system, and ΔG_{vap} is the vaporization free energy change that quantifies the interaction between ambient water vapor and adsorbed water multilayer on the particle.

Equation (S.1) represents type-I BET model, (one-parameter BET model) and does not set any limit on the number of aqueous layers that can adsorb on the aerosol particle.[3,5] To cap the number of permissible aqueous layers formation, type-II BET model (3-parameter BET model) can be implemented.[4–6] Equation (S.3) can be rearranged in terms of the water activity term, which can be expressed in terms of surface coverage as,

$$a_w = a_{w,BET} = \left(\frac{(c - \Theta(c-2)) - \sqrt{c^2(\Theta - 1)^2 + 4\Theta c}}{2\Theta(1-c)}\right) \tag{S.6}$$

The water activity defined using the BET isotherm can replace the Raoult's term in the traditional CCN activation theory (Köhler theory) for explaining the solute effect. The mathematical representation for the BET model is like the Köhler model. However, the BET model is used to describe droplet activation for sparingly soluble aerosols via water adsorption on them, as opposed to the Köhler model that describes droplet activation via complete solubility of the aerosol species. The general framework of the BET-adsorption CCN model is given as,

$$S_{BET} = a_{w,BET} \cdot exp\left(\frac{4\sigma M_w}{RT\rho_w D_{wet}}\right) \tag{S.7}$$

where a_w is the water activity term defined by Equation (S.6). The above expression is analogous to the Köhler model with the distinction between the 2 denoted only by the a_w. In the Köhler model, the water activity is expressed based on the Raoult's law that considers complete dissolution of the aerosol species in water.

Frenkel-Halsey-Hill (FHH) Adsorption Theory

Like BET, Frenkel-Halsey-Hill (FHH) theory also represents an adsorption isotherm. The mathematical formulation of the FHH isotherm is also like that of the BET isotherm in that the water activity is related to the surface coverage term. The adsorbed multilayer formation on aerosol particles is defined using the FHH adsorption isotherm that accounts for a varying adsorption potential gradient along the distance adsorbed water layer from the particle surface. In such a framework, the water activity is defined as[5,7,8],

$$a_w = a_{w,FHH} = exp\left(- A_{FHH} \cdot \Theta^{-B_{FHH}}\right) \tag{S.8}$$

where Θ is defined as the surface coverage and is defined as per Equation (S.4). A_{FHH} and B_{FHH} are FHH empirical fit parameters that describe the intermolecular forces between aerosol particle and water and in turn govern the adsorption potential. A_{FHH} determine the interactions between the particle surface and the first monolayer, and B_{FHH} determine the interactions between the surface and subsequent aqueous layers. A_{FHH} controls the net amount of water coverage on the surface and a larger value of A_{FHH} implies a greater adsorption of water. B_{FHH} controls the distance up to which the attractive interactions can affect the adsorption of subsequent aqueous layers. It has been observed that the value of B_{FHH} has a more significant role in regulating the shape of the equilibrium isotherm, as well as in confirming if the critical activation parameters for given set of particle properties exist or not.

The mathematical representation for the FHH-based CCN activation model is defined like the BET-based model and the Köhler model. This is done by substituting the water activity term in

Equation (S.7) by FHH-based activity term defined in Equation (S.8). The general framework of the FHH model can henceforth be defined as,

$$S_{FHH} = a_{w,FHH} \cdot exp\left(\frac{4\sigma M_w}{RT\rho_w D_{wet}}\right) \tag{S.9}$$

Under supersaturated conditions, for a given dry particle diameter (denoted by D_{dry}), a wet droplet diameter (denoted by D_{wet}) can exist – if the droplet grows up to this diameter at an ambient supersaturation, it activates. Physically, such a diameter at a given supersaturation defines the point beyond which the droplet grows spontaneously. Corresponding to the point of activation D_{wet} is expressed as D_c, and is called the critical diameter at the given supersaturation. Relative to the critical activation diameter, there exists a critical supersaturation for the particle. Extending Equation (S.9), the CCN activation equation based on FHH theory for estimating the water vapor saturation ratio can be expressed as,

$$S = \exp\left(- A_{FHH} \cdot \left[\frac{D_{wet} - D_{dry}}{2 \cdot D_w}\right]^{-B_{FHH}}\right) \cdot exp\left(\frac{4\sigma M_w}{RT\rho_w D_{wet}}\right) \tag{S.10}$$

where S is the ambient saturation ratio. The above expression can be used to calculate the critical supersaturation as,

$$s = \exp\left(- A_{FHH} \cdot \left[\frac{D_{wet} - D_{dry}}{2 \cdot D_w}\right]^{-B_{FHH}} + \frac{4\sigma M_w}{RT\rho_w D_{wet}}\right) - 1 \tag{S.11}$$

Equations (S.8) and (S.11) provide 2 different ways to compute species-specific FHH parameters. (S.6) is employed to fit through water adsorption measurements under subsaturated conditions.[5,9,10] Whereas Equation (S.11) is used to fit $s_c - D_{dry,50}$ data obtained from CCN activation measurements in supersaturated conditions.[8,11–13] Studies show that both the methods yield different sets of (A_{FHH}, B_{FHH}) values for a given chemical species. However, despite the discrepancies in the FHH parameters derived using different methods, agreement in the $s_c\%$ values have been observed (Hatch et al., 2019; Kumar et al., 2009) provide a simplified version of expression Equation (S.11) along with the derivative of the supersaturation with respect to D_{wet}.[8,10] The simplified version of Equation (S.11) is given as,

$$s \cong - A_{FHH} \cdot \left[\frac{D_{wet} - D_{dry}}{2 \cdot D_w}\right]^{-B_{FHH}} + \frac{4\sigma M_w}{RT\rho_w D_{wet}} \tag{S.12}$$

And based on the expression Equation (S.11), the derivative of s with respect to D_{wet} can be given as,

$$\frac{ds}{dD_{wet}} \cong \left(\frac{A_{FHH} \cdot B_{FHH}}{2 \cdot D_w} \cdot \left[\frac{D_{wet} - D_{dry}}{2 \cdot D_w} \right]^{-B_{FHH} - 1} \right) - \frac{4\sigma M_w}{RT\rho_w D_{wet}^2} \qquad \text{(S.13)}$$

Equating (A.13) to 0 for $D_{wet} = D_c$ defines the point of activation.

$$\left. \frac{ds}{dD_{wet}} \right|_{D_{wet} = D_c} \cong \left(\frac{A_{FHH} \cdot B_{FHH}}{2 \cdot D_w} \cdot \left[\frac{D_c - D_{dry}}{2 \cdot D_w} \right]^{-B_{FHH} - 1} \right) - \frac{4\sigma M_w}{RT\rho_w D_c^2} = 0 \qquad \text{(S.14)}$$

Equation (S.14) gives the critical wet diameter (D_c) which can be substituted in Equation (S.12) to obtain critical supersaturation (s_c). Following this method, theoretical activation point can be determined for particles of given dry diameters.

It is a common practice to relate the measured s_c and $D_{dry,50}$ data using power law which is generally represented as $s_c = C \cdot D_{dry,50}^{x}$, where C and x are fit parameters that depend on the measured activation data.[8,11] The utility of the power law is that FHH fit parameters, henceforth the power law fit parameters, can be determined by fitting the FHH-AT Equation (S.12) to the measured experimental CCN activation data.

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