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Supplement of

Cloud condensation nuclei activity of $CaCO_3$ particles with oleic acid and malonic acid coatings

Mingjin Wang et al.

Correspondence to: Tong Zhu (tzhu@pku.edu.cn) and Thomas F. Mentel (t.mentel@fz-juelich.de)

Experimental

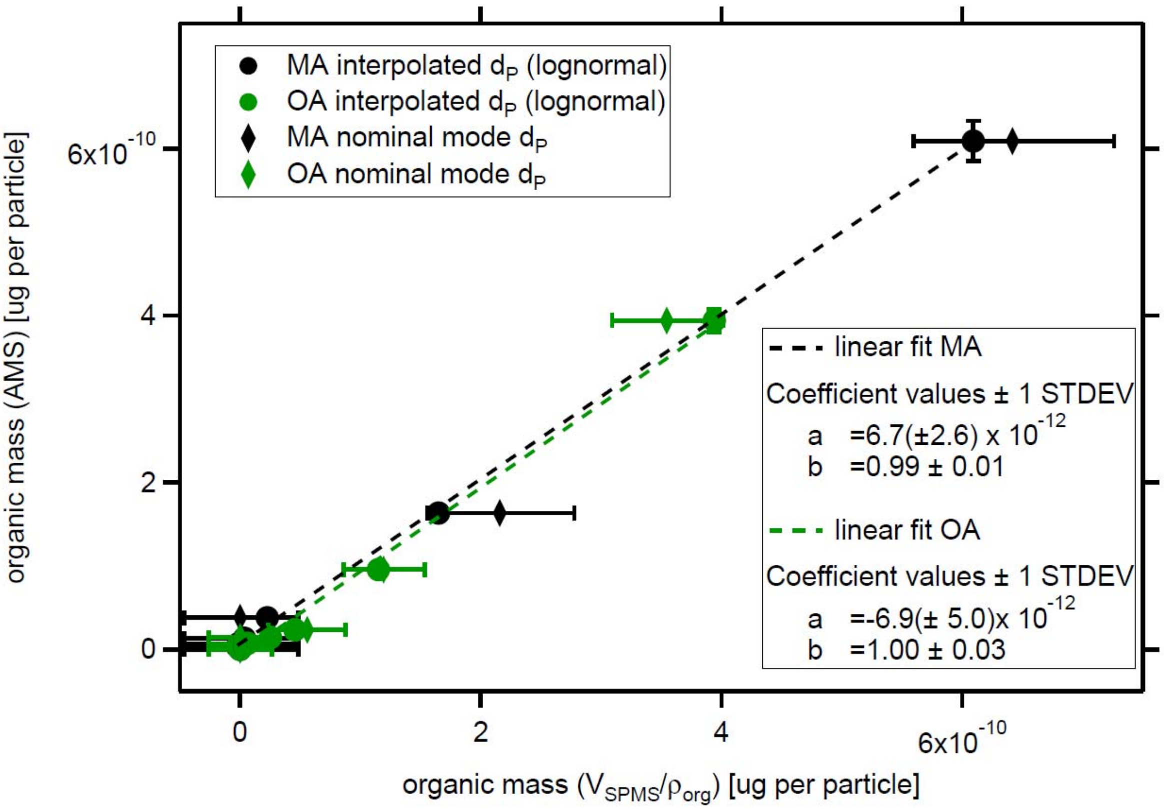

Figure S1: Linear relation between organic mass of the coating derived by AMS measurements and the organic coating mass calculated from the SMPS measurements for oleic acid coatings (green) and malonic acid coatings (black). For full circles the organic mass derived by SMPS was calculated from interpolated mode diameters given in Table 1. Error bars in y direction give the reproducibility of the AMS measurements; error bars in x direction indicate the mass span by considering the SMPS bin width for the respective nominal mode diameter. Note that the highest values must be the same as they were used to calibrate the marker *m/z* of AMS to the SMPS derived organic mass.

Koehler theory

We assume that at the critical supersaturation (SS_{crit}) the solution is ideal, i.e. water activity coefficient is close to 1, and the partial molar volume of water equals the molar volume of pure water M_w/ρ_w. Since the solubility of $CaCO_3$ in water is very low (0.00058 g/100 g water, at 298 K), while the solubility of malonic acid (MA) is quite high (62 g/100 g water at 298 K), we apply the linearized approach (e.g. Seinfeld and Pandis 2006), to predict the saturation ratio as a function of the mole solute on a insoluble core:

$$\ln\left(\frac{P_w(D_w)}{P^\circ}\right) = \frac{A}{D_w} - \frac{B}{(D_w{}^3 - d_u{}^3)} \qquad \text{(S1)}$$

In this equation A represents the Kelvin effect while B contains the solute effect:

$$A = \frac{4M_w\sigma_w}{RT\rho_w} \cong \frac{0.66}{T} \qquad (in\ \mu m) \qquad \text{(S2)}$$

$$B = \frac{6n_sM_w}{\pi\rho_w} \cong 3.44 \times 10^{13} v \times n_s \qquad (in\ \mu m^3) \qquad \text{(S3)}$$

Herein $P_w(D_w)$ is the water vapor pressure over the droplet of diameter D_w; P° is the water vapor pressure over a flat surface at the same T; d_u is the diameter of insoluble particle fraction, in our case the $CaCO_3$ core; M_w is water molecular weight; σ_w is the air-water surface tension; ρ_w is the water density; T is in K; R is the universal gas constant; n_s is solute moles = m_s/M_s, with M_s as solute molecular weight. v is the dissociation degree, i.e. the number of ions resulting from the dissociation of one solute molecule.

We neglected the little dissolvable $CaCO_3$ and considered only malonic acid molecules for the dynamic growth. The insoluble $CaCO_3$ core was set to $d_u = 0.1019\ \mu m$ as observed. We further assume that $CaCO_3$ doesn't react with malonic acid and that the surface tension of the solution at activation is that of pure water. The dissociation constants pkA$_1$ and pkA$_2$ of MA are 2.8 and 5.7 in water, respectively. So MA will partly dissociate in water and in the limit of infinite dilute solutions the dissociation degree v (van' Hoff factor) will be three for full dissociation. The moles of malonic acid coating n_s was taken from the AMS data in Table 1 and we applied v =3.

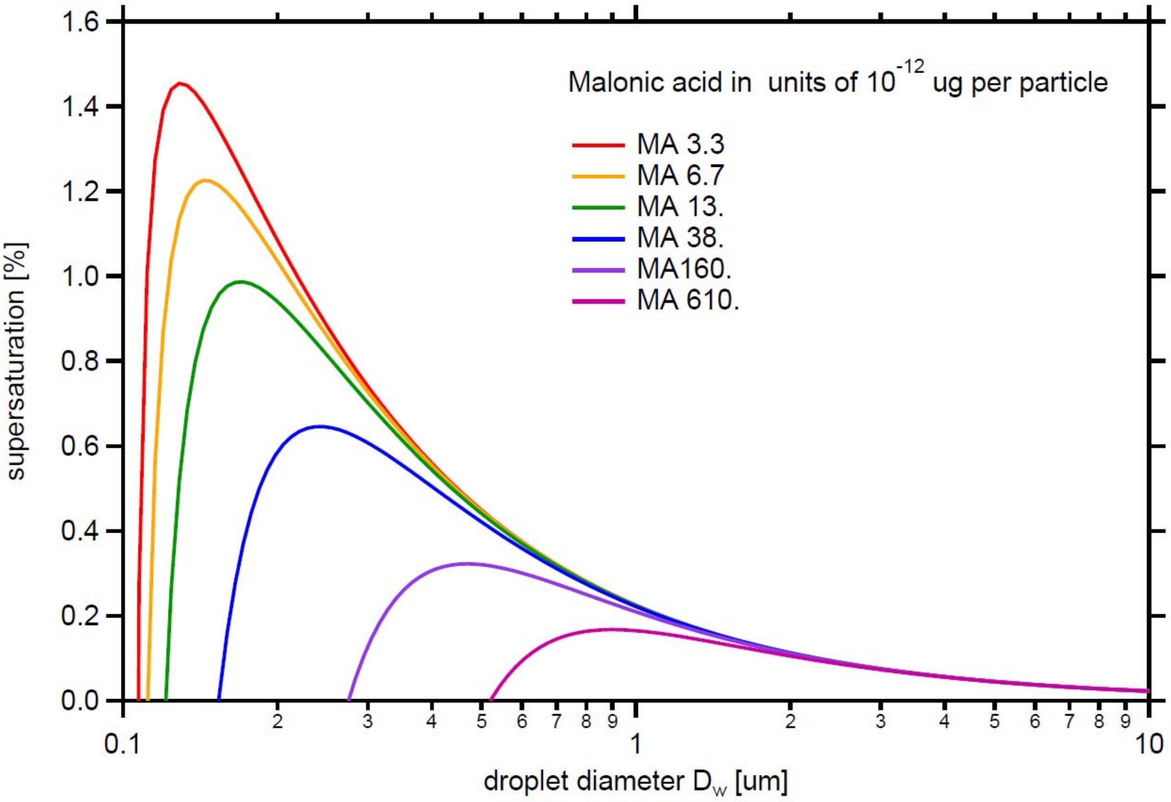

Figure S2. Variation of the equilibrium supersaturation over aqueous solution drops containing $CaCO_3$ and different mass of malonic acid at 293 K, assuming $CaCO_3$ is insoluble and doesn't react with malonic acid and the solution is dilute (water activity coefficient is close to 1). The diameter of insoluble $CaCO_3$ is 101.9 nm.

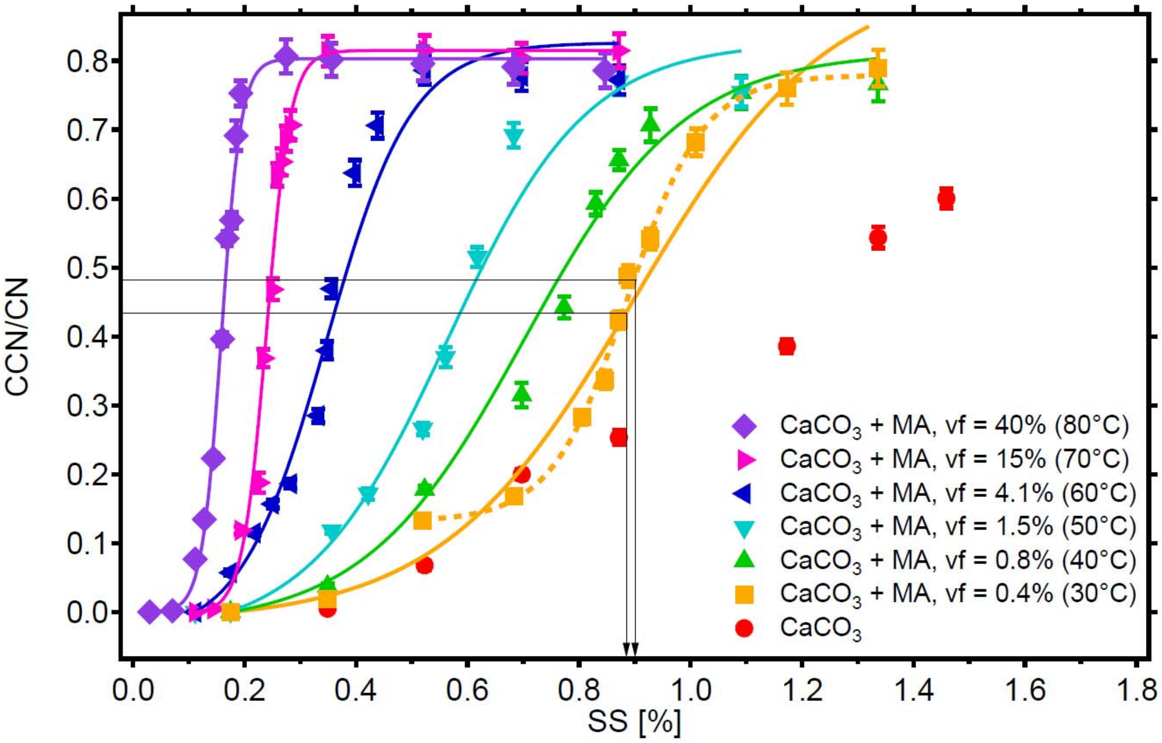

Figure S3: Systematic error introduced by neglecting the contribution of multiple charged particles in determining SS_{crit} by single sigmoidal fits. The multiple charge plateau is best recognizable for the MA coating with the smallest vf=0.4% (orange). The difference in SS_{crit} considering the plateau (0.900% dashed orange line) and neglecting it (0.887% solid orange line) is only 0.013%. The importance of the effect is largest for the smallest vf and disappears for the largest vf's.

Table S1. Koehler theory and experimental SS_{crit} and κ values of $CaCO_3$ particles with different mass of MA coating.

Dry diam. (nm)	MA per particle ($\times 10^{-12}$ μg)	Theory SS_{crit} (%)	Experimental SS_{crit} (%)	Theory κ	Experimental κ
102.0	3.3±0.3	1.44	0.900	0.0021	0.0123±0.0005
102.1	6.8±1.2	1.20	0.702	0.0048	0.0231±0.0008
102.2	13±1.8	0.97	0.564	0.0099	0.0380±0.0012
102.7	38±1.6	0.63	0.347	0.0292	0.1063±0.0023
107.8	160±8.1	0.32	0.239	0.1063	0.1907±0.0031
121.0	610±24	0.16	0.158	0.3001	0.3126±0.0062

Table S2. Properties of investigated compounds.

Name	Formula	Molecular weight (g mol^{-1})	Density (g cm^{-3})	Solubility (g/100 g water, at 298K)	Surface tension (dyn/cm)
Calcite	$CaCO_3$	100.1	2.71	0.00058	-[a]
Malonic acid	$C_3H_4O_4$	104.1	1.62	62	69[b]
Oleic acid	$C_{18}H_{34}O_2$	282.5	0.89	Very low	33[c]

a: no data
b: Surface tension of 0.01 mole fraction malonic acid aqueous solution at 298K
c: Surface tension of pure oleic acid at 293K
Lide, 2001; Yalkowsky and He, 2003; Chumpitaz et al., 1999; Hyvarinen et al., 2006.

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