



# Classifying organic materials by oxygen-to-carbon elemental ratio to predict the activation regime of Cloud Condensation Nuclei (CCN)

M. Kuwata, W. Shao, R. Leboucheiller, and S. T. Martin

School of Engineering and Applied Sciences & Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA

Correspondence to: S. T. Martin (scot\_martin@harvard.edu)

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**Abstract.** The governing highly soluble, slightly soluble, or insoluble activation regime of organic compounds as cloud condensation nuclei (CCN) was examined as a function of oxygen-to-carbon elemental ratio (O:C). New data were collected for adipic, pimelic, suberic, azelaic, and pinonic acids. Secondary organic materials (SOMs) produced by  $\alpha$ -pinene ozonolysis and isoprene photo-oxidation were also included in the analysis. The saturation concentrations  $C$  of the organic compounds in aqueous solutions served as the key parameter for delineating regimes of CCN activation, and the values of  $C$  were tightly correlated to the O:C ratios. The highly soluble, slightly soluble, and insoluble regimes of CCN activation were found to correspond to ranges of  $[O:C] > 0.6$ ,  $0.2 < [O:C] < 0.6$ , and  $[O:C] < 0.2$ , respectively. These classifications were evaluated against CCN activation data of isoprene-derived SOM (O:C = 0.69–0.72) and  $\alpha$ -pinene-derived SOM (O:C = 0.38–0.48). Isoprene-derived SOM had highly soluble activation behavior, consistent with its high O:C ratio. For  $\alpha$ -pinene-derived SOM, although CCN activation can be modeled as a highly soluble mechanism, this behavior was not predicted by the O:C ratio, for which a slightly soluble mechanism was anticipated. Complexity in chemical composition, resulting in continuous water uptake and the absence of a deliquescence transition that can thermodynamically limit CCN activation, might explain the difference in the behavior of  $\alpha$ -pinene-derived SOM compared to that of pure organic compounds. The present results suggest that atmospheric particles dominated by hydrocarbon-like organic components do not activate (i.e., insoluble regime) whereas those dominated by oxygenated organic components activate (i.e., highly soluble regime) for typical atmospheric cloud life cycles.

## 1 Introduction

The cloud condensation nuclei (CCN) activity of atmospheric particles affects particle lifetime and aging as well as their direct and indirect effects on climate (Twomey, 1977; Ramanathan et al., 2001; Stevens and Feingold, 2009). CCN activity of aerosol particles is dependent on size and chemical composition (McFiggans et al., 2006). Organic compounds are an important contributor to the CCN activity of atmospheric particles because of their abundance and hygroscopicity, although the complexity of their chemical composition challenges a systematic understanding of their effects (Novakov and Penner, 1993; Shulman et al., 1996; McFiggans et al., 2006; Jimenez et al., 2009). For instance, atmospheric organic particles have been estimated to be composed of more than a thousand compounds, yet only 10's to 100's of them are molecularly characterized (Hallquist et al., 2009; O'Brien et al., 2013). According to the Köhler theory, various properties of each organic compound in a particle affect CCN activity, including solubility, molecular weight, density, and non-ideality in aqueous solution (Shulman et al., 1996; Raymond and Pandis, 2002; McFiggans et al., 2006). Those complexities hinder accurate predictions of the contribution of organic compounds to the CCN activity of aerosol particles.

In the atmosphere, variability in size distribution is large, serving as a significant regulator of CCN number concentration (Dusek et al., 2006). Detailed chemical composition, especially the fraction of water-soluble materials, controls activation threshold diameter. Predicting the water solubility of atmospherically relevant compounds from measurable and predictable parameters is therefore important (Kuwata et al., 2008).

The CCN activity of atmospherically relevant pure organic compounds has been investigated in many studies (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Prenni et al., 2001; Hartz et al., 2006; Hings et al., 2008). These studies demonstrate that the experimental results for highly water soluble compounds are well explained by the Köhler theory. By comparison, data for slightly soluble compounds are still difficult to interpret, in part because of significant variability in experimental data. For instance, the reported experimental results for the CCN activity of adipic acid particles vary widely, which is perhaps related to artifacts associated with particle generation methods (Hartz et al., 2006; Rissman et al., 2007; Hings et al., 2008). Data discrepancies have also been reported for pinonic acid (Raymond and Pandis, 2002; Hartz et al., 2006). These uncertainties should be reduced and ideally eliminated for accurate understanding of the effects of organic components on the CCN activity of atmospheric particles.

Secondary organic material (SOM), composed in large part of the low-volatility fraction of the oxidation products of volatile organic compounds, is one important subclass of atmospheric organic compounds and can be highly CCN active (Hartz et al., 2005; VanReken et al., 2005; King et al., 2007; Wex et al., 2009; Kuwata et al., 2011). Both laboratory and ambient SOM is composed of so many different compounds, uncharacterized both in identity and quantity, that the CCN activity of the composite particle cannot be predicted based on first-principle using molecular composition. An alternative approach for complex compositions is to base CCN activity on an aggregate quantity, such as the oxygen-to-carbon elemental ratio (O : C) of the organic material. The O : C ratio is a parameter that can be both defined and measured for complex mixtures, as well as pure compounds, and initial studies have empirically demonstrated positive correlations between O : C ratio and CCN activity in some cases (Chang et al., 2010; Kuwata et al., 2011; Lambe et al., 2011). A detailed understanding of the relationship, however, meaning one founded in theory and complemented by laboratory data, is still needed. This type of rational explanation can then be used to evaluate the capabilities, the limitations, and the possible extensions of the positive correlations reported between O : C ratio and CCN activity.

In the present study, existing data are combined with new data for the CCN activities of pure organic compounds. A new particle generation system is developed for the study of slightly soluble compounds. The CCN activities of pure compounds, including both literature data and the new experimental results of this study, are analyzed with respect to their elemental ratios to establish a relationship between CCN activity and oxygen-to-carbon elemental ratio. The relationship between saturation water solubility and O : C ratio is also investigated. These two relationships are combined to relate the regime of CCN activation to the O : C elemental ratio. Finally, data for SOM CCN activity and O : C

ratio are used to test for differences between the behavior of pure compounds and that of a complex mixture of myriad compounds

## 2 Theory

### 2.1 Köhler equation

The hygroscopic growth and subsequent CCN activation of an aerosol particle can be described by the Köhler equation (Köhler, 1936; Seinfeld and Pandis, 2006):

$$\ln s = \frac{4\sigma M_w}{RT\rho_w d} + \ln a_w \quad (1)$$

Quantities include the saturation ratio  $s$  of water vapor in the gas phase, the activity  $a_w$  of water in the particle phase, the surface tension  $\sigma$  of water at the particle-gas interface, the molecular weight  $M_w$  of water, the universal gas constant  $R$ , the temperature  $T$ , the material density  $\rho_w$  of liquid water, and the diameter  $d$  of the particle following water uptake. The first quantity of the RHS of Eq. (1) is referred to as the Kelvin term and the second quantity is known as the Raoult term. For CCN activation, supersaturation  $S$  is defined as  $S = s - 1$ . The critical supersaturation  $S^*$  of a particle is the global maximum of  $S(d)$  with respect to  $d$ . Particles activate as CCN for any environment or process that satisfies the thermodynamic condition  $S > S^*$ , although in addition to thermodynamics activation kinetics can sometimes also limit CCN activation (Ruehl et al., 2008).

For an aerosol particle constituted by  $i$  different chemical components (plus water) and for water activity expressed by the molal osmotic coefficient  $\varphi$  (Robinson and Stokes, 2002), Eq. (1) is re-written as follows (Raymond and Pandis, 2002; Seinfeld and Pandis, 2006; Petters and Kreidenweis, 2008):

$$\ln s = \frac{4\sigma M_w}{RT\rho_w d} - \frac{\varphi d_0^3}{d^3 - d_0^3} \sum_i v_i f_i \varepsilon_i \frac{M_w \rho_i}{M_i \rho_w}$$

for  $\varepsilon_i = \text{Min} \left[ 1, \left( \frac{d^3}{d_0^3} - 1 \right) \frac{C_i}{f_i} \right]$  (2)

Quantities include the solute molecular weight  $M_i$ , the solute material density  $\rho_i$  in pure form, the stoichiometric number  $v_i$  of ions or molecules for ideal solute dissolution in water, the volume fraction  $f_i$  of component  $i$  in the particle in the absence of water, the dissolved solute fraction  $\varepsilon_i$ , the volume-based concentration ratio  $C_i$  ( $v/v$ ) of the pure compound in a saturated aqueous solution, and the diameter  $d_0$  of the particle in the absence of water uptake. Independent behavior is assumed for the  $i$  components in aqueous form, including the absence of mutual effects on solubility and non-ideality. The molal osmotic coefficient can be calculated using semi-empirical methods (Clegg and Seinfeld, 2006). The case of  $\varepsilon_i = 1$  corresponds to fully solubilized material and  $0 < \varepsilon_i < 1$  indicates partially solubilized material.

Depending on  $C$ , four different cases can be considered with respect to  $S^*$ : (1) infinitely soluble, (2) highly soluble, (3) slightly soluble, and (4) insoluble (Fig. 1). Infinitely soluble particles are miscible with water, and in this case  $\varepsilon_i$  is unity (Fig. 1, purple line). Highly soluble particles deliquesce at a lower supersaturation than  $S^*$  (Fig. 1; red line), meaning  $\varepsilon$  is again unity with respect to calculation of  $S^*$ . For the infinitely and highly soluble cases, the value of  $S^*$  depends strongly on  $M_i$  (Petters et al., 2009a). For the case of slightly soluble particles, deliquescence occurs at high  $a_w$ , typically very close to unity (e.g.,  $> 0.97$ ) (Kreidenweis et al., 2006). Because of the Kelvin effect, the implication for particles of typical CCN sizes is that deliquescence occurs only in supersaturated environments (Fig. 1; blue line). For the case of insoluble particles,  $a_w$  equals unity, and the value of  $S^*$  depends solely on the Kelvin effect (Fig. 1; black line). The behaviors described for these four cases correspond to the following domains of  $C$ : (1) infinitely/highly soluble ( $C > 10^{-1}$ ), (2) slightly soluble ( $10^{-4} < C < 10^{-1}$ ), and (3) insoluble ( $C < 10^{-4}$ ) (Petters and Kreidenweis, 2007; Sullivan et al., 2009).

In the case of  $\varepsilon_i < 1$  for all  $i$ , Eq. (2) simplifies as follows:

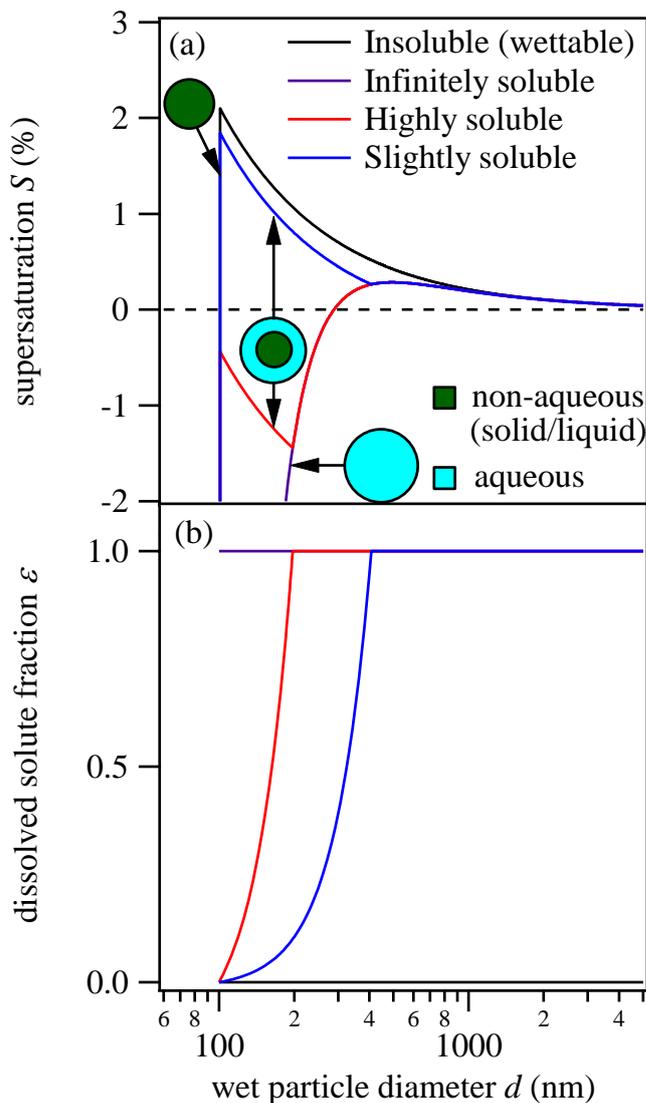
$$\ln s = \frac{4\sigma M_w}{RT\rho_w d} - \varphi \sum_i \left[ v_i C_i \frac{M_w \rho_i}{M_i \rho_w} \right] \quad (3)$$

The Raoult term depends on chemical composition but not on  $d_0$  or  $d$  because the aqueous phase is saturated (Raymond and Pandis, 2002). The associated physical description is that the particle consists of one phase of saturated aqueous solution and one phase of undissolved material. This equation is applicable to the case of CCN activation of slightly soluble particles:  $S$  of initial deliquescence corresponds to  $S^*$  because the diameter of the two-phase particle is continuously increasing and hence the Kelvin effect is continuously decreasing, even while  $a_w$  remains constant during the continuous dissolution process of initial to final deliquescence. For a deliquescence water activity  $a_{w,D}$  of a slightly soluble particle, the value of  $S^*$  is then given by the following equation.

$$\ln(S^* + 1) = \frac{4\sigma M_w}{RT\rho_w d} + \ln a_{w,D} \quad (4)$$

## 2.2 Single parameter representing CCN activity

The foregoing equations can be used to calculate  $S^*$  so long as all the parameters are accurately known. The parameter values, however, are not always known, especially for atmospheric particles as well as for laboratory-generated SOM. An alternative representation of CCN activation is represented using a lumped-sum single parameter  $\kappa$ , which is approximately related to the fundamental quantities of Eqs. (1) to (4) as follows for highly soluble materials (Petters



**Fig. 1.** Examples of Köhler curves for infinitely soluble (purple), highly soluble (red), slightly soluble (blue), and insoluble (black) particles. The calculations were conducted for input parameters of  $\{M, \rho, \sigma, d_0\} = \{0.146 \text{ kg mol}^{-1}, 1362 \text{ kg m}^{-3}, 0.072 \text{ J m}^{-2}, 100 \text{ nm}\}$ . The value of  $C$  was taken as 0.15 (v/v) for highly soluble particles and 0.015 (v/v) for slightly soluble particles. Further explanation is provided in the text.

and Kreidenweis, 2007):

$$\kappa = \left( v\varphi \frac{M_w}{\rho_w} \right) \left( \frac{\rho_{\text{org}}}{M_{\text{org}}} \right) \quad (5)$$

This equation demonstrates that  $\kappa$  is proportional to both  $1/M_{\text{org}}$  and  $\rho_{\text{org}}$ . The value of  $\kappa$  varies from 0 for insoluble materials (e.g., oleic acid) to 1.3 for highly soluble materials (e.g., sodium chloride).

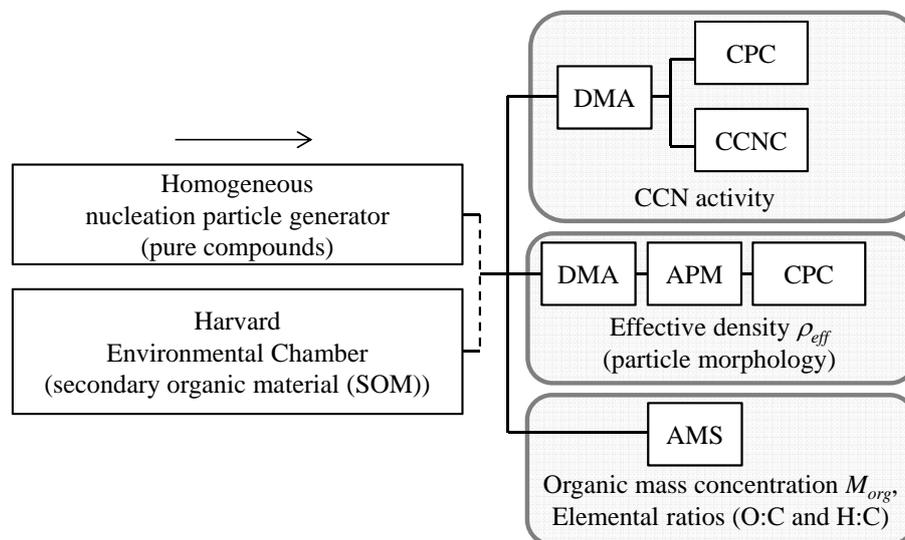
**Table 1.** Properties of tested organic compounds.

Compound	Formula	$M_{\text{org}}$ (kg mol <sup>-1</sup> )	O:C	H:C	$\rho^{\text{a}}$ (kg m <sup>-3</sup> )	$C^{\text{b}}$ (v/v)	$\sigma^{\text{a,c}}$ (J m <sup>-2</sup> )
adipic acid	C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>	0.146	0.67	1.67	1362	$1.8 \times 10^{-2}$	0.066
pimelic acid	C <sub>7</sub> H <sub>12</sub> O <sub>4</sub>	0.160	0.57	1.71	1321	$4.9 \times 10^{-2}$	0.049
suberic acid	C <sub>8</sub> H <sub>14</sub> O <sub>4</sub>	0.174	0.50	1.75	1272	$1.8 \times 10^{-3}$	0.055
azelaic acid	C <sub>9</sub> H <sub>16</sub> O <sub>4</sub>	0.188	0.44	1.78	1251	$1.4 \times 10^{-3}$	0.059
pinonic acid	C <sub>10</sub> H <sub>16</sub> O <sub>3</sub>	0.184	0.30	1.60	1169	$5.5 \times 10^{-3\text{a}}$	0.053

<sup>a</sup> Hartz et al. (2006).

<sup>b</sup>  $C$  is from the empirical fit of experimental data (25 °C, Appendix A1), except for pinonic acid.

<sup>c</sup> Values are for saturated aqueous solutions.



**Fig. 2.** Experimental setup. Abbreviations: TSI Differential Mobility Analyzer (DMA); TSI Condensation Particle Counter (CPC); DMT Cloud Condensation Nuclei Counter (CCNC); KANOMAX Aerosol Particle Mass Analyzer (APM); and Aerodyne Aerosol Mass Spectrometer (AMS).

For a particle of dry diameter  $d_0$  and parameter  $\kappa$ , the critical supersaturation is given as follows:

$$\kappa d_0^3 \ln^2 S^* = \frac{4}{27} \left( \frac{4\sigma M_w}{RT\rho_w} \right)^3 \quad (6)$$

Although  $\sigma$  is in principle a function of both chemical composition and solute concentration, such information is rarely available, and the value of water is taken by definition for  $\kappa$ . Other quantities on the RHS of Eq. (6) are taken for 300 K for the definition of  $\kappa$ . The value of  $\kappa$  directly relates  $d_0$  and  $S^*$ , and this relationship is obtained either by theoretical or experimental approaches. The utility of  $\kappa$  is that it is approximately constant for variable  $d_0$ , at least for some ideal cases.

### 3 Experimental

The experimental setup is represented in Fig. 2. In overview, particles produced either in a custom evaporation-

condensation generator or in the Harvard Environmental Chamber (HEC) were characterized for their CCN activity and effective density  $\rho_{\text{eff}}$  (Shilling et al., 2008; Chen et al., 2011; Kuwata and Martin, 2012b). Particle organic mass concentrations  $M_{\text{org}}$  as well as elemental ratios were also measured using a high-resolution Aerodyne Aerosol Mass Spectrometer (AMS) (DeCarlo et al., 2006).

In a first set of experiments, particles of five pure organic compounds were tested, including adipic, pimelic, suberic, azelaic, and pinonic acid (Table 1) (Sigma-Aldrich, purity > 98 %). The chemicals were received as powders, and aerosol particles were produced by evaporation of the powders at elevated temperature (> 373 K, depending on compounds), homogeneous nucleation of new particles from the hot vapors, and condensation and coagulation growth of those particles (cf. Supplement). The particle generator consisted of a heated U-tube (inner diameter of 10 mm) and an air-cooled condenser (Kuwata and Martin, 2012b). The chemicals were placed at the bottom of the U-tube, which was encased by a ribbon heater (Omega Engineering Inc.

**Table 2.** Summary of experimental conditions for the HEC experiments.

Exp	Reaction conditions		Seed particles		Measured quantities			
	Precursor compound	relative humidity (%)	diameter (nm)	phase	organic particle mass concentration ( $\mu\text{g m}^{-3}$ )*	H : C	O : C	$\kappa$
1	$\alpha$ -pinene	40	30	dry	1.4	1.40	0.48	0.10
2	$\alpha$ -pinene	40	30	dry	5.7	1.43	0.44	0.10
3	$\alpha$ -pinene	40	30	dry	10	1.43	0.41	0.11
4	$\alpha$ -pinene	40	30	dry	25	1.46	0.40	0.10
5	$\alpha$ -pinene	40	30	dry	37	1.47	0.38	0.11
6	isoprene	40	30	dry	37	1.86	0.71	0.17
7	isoprene	40	30	wet	19	1.84	0.72	0.16
8	isoprene	60	30	dry	15	1.79	0.72	0.15
9	isoprene	60	30	wet	18	1.84	0.69	0.16

\* Not corrected for bag wall loss (Shilling et al., 2008).

FGS0031) to induce vaporization. Pure air (AADCO model 737) continuously flowed through the U-tube. A flow rate of 1 to 10 Lpm was used depending on experimental conditions. Higher (lower) flow rates favored the production of smaller (larger) particles. Vapors of the organic compounds were transferred from the evaporator to the condenser in the pure air flow. New particle formation occurred in the condenser by homogeneous nucleation, and the fresh nuclei grew downstream by coagulation and condensation mechanisms. Particles exiting the condenser were mixed with pure air to regulate number concentration to no more than  $3000\text{ cm}^{-3}$  (Lathem and Nenes, 2011). This particle generation method had the advantage of producing crystalline, solid particles of high purity (Hings et al., 2008; Biskos et al., 2009; Kuwata and Martin, 2012b). For instance, AMS analysis of adipic acid particles produced by atomization of an aqueous solution showed the presence of significant ammonia even with extensive efforts to purify the water. By comparison, AMS analysis of the evaporation-condensation particles had an absence of any significant ammonia peak (Kuwata and Martin, 2012b).

A second set of experiments focused on particles of secondary organic material extracted from the outflow of the Harvard Environmental Chamber. Methods were similar as described previously (Kuwata et al., 2011, 2012). Briefly, SOM produced by  $\alpha$ -pinene dark ozonolysis or isoprene photooxidation condensed onto the surface of ammonium sulfate seed particles, which then continued to grow by additional SOM condensation (Kuwata and Martin, 2012a). Prior to entering the continuous-flow chamber, the seed particles were size-classified by a differential mobility analyzer (DMA) to an electric mobility diameter of 30 nm (+1 charge). The particles exiting the chamber varied in diameter from 30 to 300 nm depending on an individual particle residence time (0 to 12 h). Table 2 presents a summary of the different conditions used for the conducted experiments.

Particles from both sets of experiments were characterized for the single parameter  $\kappa$  that quantified CCN activity and for particle effective density  $\rho_{\text{eff}}$ . Measurement methods and calibration procedures followed those described in Kuwata and Kondo (2009) and Kuwata et al. (2011). In brief, after passage through a diffusion dryer (only for SOM particles) and variable size selection by a DMA (TSI model 3071), the number fraction of CCN active particles was quantified by taking the ratio of the number concentration of a CCN counter (CCNC) (Roberts and Nenes, 2005) set to a specific supersaturation  $S$  (0.2 to 1.0 %) to the total number concentration of a condensation particle counter (CPC, TSI model 3022). The CCNC was calibrated using ammonium sulfate particles. The maximum temperature inside of the CCNC during the course of experiments was 311 K at the bottom of the column, corresponding to the highest  $S$  (1 %). The CCN activation curves (i.e., the number fraction of CCN active particles plotted against particle diameter) were fit by sigmoid functions, and the midpoint diameter was taken as  $d_0$  and used to determine the value of  $\kappa$  (Kuwata et al., 2011). The volume fraction of the SOM was greater than 0.95 for the analyzed particles (i.e., > 80 nm), and a correction was included in the analysis based on volume additivity between sulfate (< 5 %) and SOM (Kuwata et al., 2011). Particle effective density  $\rho_{\text{eff}}$  was measured using a DMA in serial connection to an aerosol particle mass analyzer (APM) (Ehara et al., 1996; McMurry et al., 2002). The value of  $\rho_{\text{eff}}$  is smaller than material density for particles of non-spherical shape (Kuwata and Kondo, 2009). The value of  $\rho_{\text{eff}}$  was used to obtain accurate values of volume-equivalent diameter  $d_{\text{ve}}$  (i.e.,  $d_0$ ) for interpretation of the CCN data in the experiments that used pure compounds.

**Table 3.** Values of single parameter  $\kappa$  for organic compounds tested in this study. Raw data are presented in the Supplement.

Compound		$\kappa^a$
Adipic acid	experiment	0.002–0.003 (this study) 0.097 (Cruz and Pandis, 1997) 0.030 (Corrigan and Novakov, 1999) 0.013 (Prenni et al., 2001) 0.01–0.03 (Raymond and Pandis, 2002) 0.004–0.01 (Broekhuizen et al., 2004) 0.003 (Hartz et al., 2006) 0.05–0.08 (Rissman et al., 2007) 0.003–0.22 (Hings et al., 2008)
	theory	0.16 (case 1 <sup>b</sup> ) 0.001–0.004 (case 2 <sup>c</sup> )
Pimelic acid	experiment	0.14–0.16 (this study) 0.14 (Hartz et al., 2006) 0.15 (Frosch et al., 2010)
	theory	0.15 (case 1 <sup>b</sup> ) 0.03 (case 2 <sup>c</sup> )
Suberic acid	experiment	0.001 (this study) 0.001 (Hartz et al., 2006)
	theory	0.13 (case 1 <sup>b</sup> ) 0.002–0.003 (case 2 <sup>c</sup> )
Azelaic acid	experiment	0.02–0.04 (this study) 0.02 (Hartz et al., 2006)
	theory	0.12 (case 1 <sup>b</sup> ) 0.001–0.002 (case 2 <sup>c</sup> )
Pinonic acid	experiment	0.01 (this study) 0.1 (Raymond and Pandis, 2002) 0.009–0.04 (Hartz et al., 2006)
	theory	0.11 (case 1 <sup>b</sup> ) 0.001–0.003 (case 2 <sup>c</sup> )

<sup>a</sup> Equation (6) was used to calculate the values assuming a value for  $\sigma$  of that of water ( $0.072 \text{ J m}^{-2}$ ).

<sup>b</sup> Equation (2) was employed to calculate  $S^*$ , assuming that dissolved solute fraction  $\varepsilon$  is always unity, and the value of surface tension  $\sigma$  is equal to that of water.

<sup>c</sup> Equation (2) was employed to calculate  $S^*$ , using the solubility data at 25 °C, and the surface tension  $\sigma$  of saturated aqueous solution (Table 1).

## 4 Results

### 4.1 Pure compounds

The CCN activation curves are presented in the Supplement (Shao, 2012). The  $\kappa$  and  $a_{w,D}$  values were obtained by analysis of the data using Eqs. (4) and (6). Adipic, suberic, azelaic, and pinonic acids activated as slightly soluble particles. By comparison, pimelic acid activated as a highly soluble particle. The experimentally determined  $\kappa$  values along with theoretical predictions and literature data are listed in Table 3.

#### 4.1.1 Adipic acid

The CCN activity of adipic acid particles has been intensely investigated, yet the experimental data of different studies are inconsistent, with  $\kappa$  ranging from 0.003 to 0.22 (Cruz

and Pandis, 1997; Corrigan and Novakov, 1999; Prenni et al., 2001; Raymond and Pandis, 2002; Broekhuizen et al., 2004; Hartz et al., 2006; Rissman et al., 2007; Hings et al., 2008). Particle phase as well as impurities are possibly responsible for the variability among studies (Rissman et al., 2007; Hings et al., 2008). Our present experimental result for  $\kappa = 0.002$  to 0.003 agrees with the theoretical prediction, corresponding to the lower edge of literature data (Table 3). The value of  $a_{w,D}$  estimated from the experimental data agrees with that reported by Chan et al. (2008) as well as that predicted from the value of  $C$ , at least within the uncertainty of the measurements (Table 4) (Gaivoronskii and Granzhan, 2005). This agreement indicates the merit in using vaporization-condensation method in generating organic aerosol particles, which minimizes contaminations and ambiguity in phase by avoiding interaction with water molecules (Kuwata and Martin, 2012b).

#### 4.1.2 Pimelic acid

The value of  $\kappa = 0.14$  to 0.16 observed for pimelic acid particles is similar to values reported by previous studies (Hartz et al., 2006; Frosch et al., 2010). The combined results indicate that pimelic acid particles are highly soluble. By comparison, theoretical calculations anticipate slightly soluble particles because  $C = 0.04$  at 293 K (Hartz et al., 2006).

Some technical issues associated with CCNC instrumentation, as well as particle production methods, must be considered in elucidating possible reasons for the discrepancy among the theoretical prediction and experimental observations. There are temperature gradients inside the instruments that can significantly influence CCN activation for compounds that have high sensitivity with respect to temperature-dependent solubility (Asa-Awuku et al., 2009; Christensen and Petters, 2012). Apelblat and Manzurola (1989) reported a significant temperature dependence for the solubility of pimelic acid, more so than for the other studied acids (Appendix A1). The highest temperature in the CCNC during the measurement of pimelic acid particles was 303 K, corresponding to the lower section of the instrument. At this temperature, the value of  $C = 0.06$  borders between highly and slightly soluble, leading to a hypothesis that the elevated temperature in the instrument altered the CCN activation regime of the pimelic acid particles. CCN activity of pimelic acid particles is in particular sensitive to temperature because the solubility at room temperature is on the border between slightly and highly soluble cases. Temperature dependences in solubility have also been investigated for other organic compounds, yet such regime shifts were not observed for these cases (Appendix A1). A systematic experiment on the temperature dependence is motivated for confirming this explanation for pimelic acid (Christensen and Petters, 2012). Another possibility is that impurities such as ammonia could affect solubility, as in the case of adipic

**Table 4.** Values of water activity  $a_{w,D}$  of deliquescence based on CCN activation data. Data from Chan et al. (2008) are listed for comparison.

Compound	$a_{w,D}$ (this study) <sup>a</sup>	$a_{w,D}$ (ideal solution) <sup>c</sup>	$a_{w,D}$ (Chan et al., 2008) <sup>d</sup>
Adipic acid	0.998–0.999	0.994–0.998 (20–40 °C)	0.998
Pimelic acid	< 0.988 <sup>b</sup>	0.986–0.994 (20–37 °C)	0.995
Suberic acid	~ 1	0.999 (20–40 °C)	0.999
Azelaic acid	0.988–0.996	0.999 (20–40 °C)	0.999
Pinonic acid	0.995–0.997	0.999	

<sup>a</sup> Calculated using equation 4 for the surface tension of a saturated solution (Table 1).

<sup>b</sup> The value corresponds to the maximum estimate for highly soluble activation mechanism.

<sup>c</sup> Calculated using Eq. (A2).

<sup>d</sup> Chan et al. (2008) measured  $a_{w,D}$  at 23 °C for a stated uncertainty of  $\pm 0.003$  by the experimental approach of measuring the water activity of saturated aqueous solutions.

acid (Hings et al., 2008; Kuwata and Martin, 2012b). Other factors, such as particle morphology, changes in surface tension at elevated temperature, or non-ideality of solution, might also influence the activation.

#### 4.1.3 Suberic acid

The experimental result of  $\kappa = 0.001$  for suberic acid is well explained as slightly soluble, consistent with the literature data (Table 3) (Hartz et al., 2006). The derived value of  $a_{w,D}$  is approximately unity, consistent with the measurements made for bulk solutions (Table 4).

#### 4.1.4 Azelaic acid

The measured value for  $\kappa$  was 0.02 to 0.03 for azelaic acid, in agreement with the literature (Hartz et al., 2006). This value characterizes a slightly soluble material. It is higher than the theoretically predicted value of 0.001–0.002 based on solubility data. Correspondingly,  $a_{w,D} = 0.988$  to 0.996, as estimated from the experimental result, is smaller than  $a_{w,D} = 0.999$  as reported in the literature and as predicted from solubility data (Chan et al., 2008). Uncertainties in the experiment, as well as uncertainties in the input parameters for the theoretical calculation, must be considered to fully understand the CCN activity of the azelaic acid particles (i.e., as listed above for pimelic acid).

#### 4.1.5 Pinonic acid

The experimental results show that pinonic acid activates in the slightly soluble regime (Table 3). This result agrees with that of Hartz et al. (2006) but contradicts the report of Raymond and Pandis (2002). Particle phase appears to affect the CCN activity of this compound, as is the case for other compounds such as adipic acid (Hartz et al., 2006). The experimentally determined  $\kappa$  value of 0.01 is higher than the theoretical prediction of  $\kappa = 0.001$  to 0.003. Correspondingly, as for azelaic acid,  $a_{w,D} = 0.995$  is smaller than  $a_{w,D} = 0.999$  as reported in the literature (Table 3 and 4).

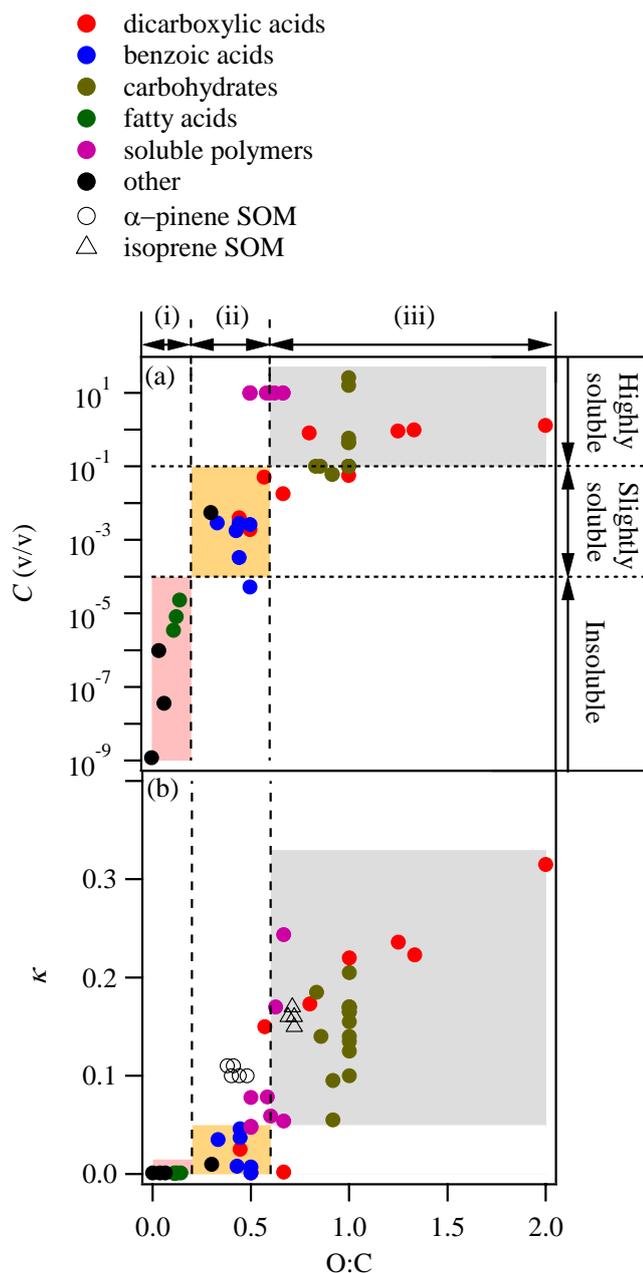
## 4.2 SOM particles

The  $\kappa$ , O:C, and H:C values obtained by measurement of  $\alpha$ -pinene-derived and isoprene-derived SOM particles are listed in Table 2. The results for the  $\alpha$ -pinene SOM particles are discussed in detail by Kuwata et al. (2011), for which  $\kappa = 0.1$  is obtained in agreement with literature (King et al., 2009; Wex et al., 2009; Frosch et al., 2011). For isoprene-derived SOM particles,  $\kappa$  of 0.15–0.17 was obtained, irrespective of the seed particle phase and the RH in the chamber. The obtained  $\kappa$  value is in agreement with literature reports ( $\kappa = 0.12 \pm 0.06$ ) (King et al., 2010; Engelhart et al., 2011; Lambe et al., 2011). The variability in the literature reports might be related to different chemical aging processes (Engelhart et al., 2011; Lambe et al., 2011). Elemental ratios of isoprene SOM are consistent with those reported by Chen et al. (2011). The results were not sensitive to seed particle phase as well as RH, at least for our experimental data set.

## 5 Discussion

### 5.1 Relationship of C to O:C

Plots of  $C$  and  $\kappa$  versus O:C are shown in Fig. 3 for the investigated compounds, including lines that demarcate highly soluble, slightly soluble, and insoluble regimes (Table 5; Appendix A2). The sources of the original data set include this study as well as literature (Corrigan and Novakov, 1999; Raymond and Pandis, 2002; Hori et al., 2003; Pradeep Kumar et al., 2003; Hartz et al., 2006; Rosenorn et al., 2006; Shilling et al., 2007; Petters et al., 2009a). In Fig. 3a of  $C$  versus O:C, there is a trend of increasing  $C$  for greater O:C. For compounds of O:C < 0.2, all of the investigated compounds are insoluble based on  $C$ . For  $0.2 < O:C < 0.6$ , most compounds are slightly soluble, although water soluble polymers are an exception. Those polymers have large H:C, suggesting the use of H:C in conjunction with O:C for more accurate estimates of  $C$

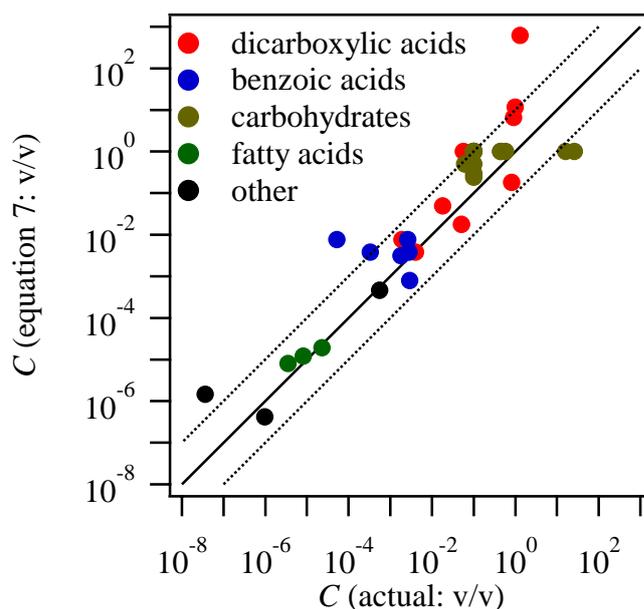


**Fig. 3.** Relationship of O:C ratio to (a)  $C$  and (b)  $\kappa$ . The colored areas in the panels highlight clustering among insoluble, slightly soluble, and highly soluble compounds. Compounds are listed in the Supplement.

(cf. Appendix A2). For O:C > 0.6, most compounds are highly soluble.

The following equation empirically developed in the present study predicts  $C$  from O:C for the tested compounds:

$$\ln C = 20 \left[ (\text{O} : \text{C})^{0.402} - 1 \right] \quad (7)$$



**Fig. 4.** Comparison of predicted  $C$  (i.e., by O:C ratio in Eq. 7) to its actual value. The solid line denotes a 1 : 1 line. The dashed lines correspond to 10-fold differences from the predictions of Eq. (7). The figure omits soluble polymers because they are miscible with water.

Figure 4 compares  $C$  of the tested compounds with the predictions from Eq. (7). The values of  $C$  for most of the tested compounds are predicted within an uncertainty of one order of magnitude, which is acceptably accurate considering that  $C$  varies by ten orders of magnitudes. The observed correlation between  $C$  and O:C can be expected. Functional groups containing oxygen (e.g., -OH, -COH, and -COOH) increase  $C$ , as demonstrated in group contribution methods for predicting  $C$  (Klopman et al., 1992).

## 5.2 Relationship of $\kappa$ to O:C

Figure 3b shows the relationship between  $\kappa$  and O:C. There are no CCN-active compounds for O:C < 0.2, as explained by the low values of  $C$  (i.e., insoluble regime). For  $0.2 < \text{O} : \text{C} < 0.6$ , most compounds have low  $\kappa$  values (i.e.,  $\kappa < 0.05$ ) in correspondence to their slightly soluble values of  $C$ , i.e., as is consistent with the predictions from Köhler theory. CCN activation of these compounds occurs at deliquescence (i.e., the activation is limited thermodynamically by deliquescence) (Kreidenweis et al., 2006). The  $\kappa$  values of synthetic polymers are an exception, having relatively high values of  $0.05 < \kappa < 0.1$ , which is explained by their high water solubility. For O:C > 0.6, compounds are highly CCN active, having  $\kappa > 0.1$ , as consistent with values of  $C$  in the highly soluble regime. These observations point to a relationship between CCN activation and the O:C value as (i) insoluble (O:C < 0.2),

**Table 5.** Summary of compounds employed for Fig. 3. The complete list is available in the Supplement.

Chemical family	O : C	H : C	$M_{\text{org}}$ (kg mol <sup>-1</sup> )	C (v/v)	$\kappa$
Dicarboxylic acids	0.44–2.00	1.00–1.78	0.090–0.188	10 <sup>-3</sup> –10 <sup>0</sup>	0.001–0.32
Benzoic acids	0.33–0.50	0.75–0.89	0.138–0.180	10 <sup>-5</sup> –10 <sup>-3</sup>	0.001–0.037
Carbohydrates	0.83–1.00	1.60–2.50	0.118–0.342	~ 10 <sup>-1</sup>	0.06–0.21
Fatty acids	0.11–0.14	1.89–2.00	0.228–0.284	10 <sup>-6</sup> –10 <sup>-5</sup>	~ 0.001
Water-soluble <sup>a</sup> polymers	0.50–0.67	1.33–2.33	0.150–2.000	miscible	0.05–0.24
Other <sup>b</sup>	0–0.30	1.60–2.13	0.184–0.387	10 <sup>-9</sup> –10 <sup>-3</sup>	0.001–0.01

<sup>a</sup> Mostly polymers of ethylene glycol, as reported by Petters et al. (2009a).

<sup>b</sup> Pinonic acid, hexadecane, hexadecanol, and cholesterol.

(ii) slightly soluble ( $0.2 < \text{O} : \text{C} < 0.6$ ), or (iii) highly soluble ( $0.6 < \text{O} : \text{C}$ ) (Figs. 3 and 5).

For highly soluble particles, CCN activity is dominantly controlled by molar volume, which is determined by both  $\rho_{\text{org}}$  and  $1/M_{\text{org}}$  (Eq. 5) (Petters et al., 2009a). Kuwata et al. (2012) developed a method to predict  $\rho_{\text{org}}$  using O : C and H : C ratios. According to the method,  $\rho_{\text{org}}$  is higher for highly oxygenated compounds. Even so, the range in  $\rho_{\text{org}}$  values for O : C > 0.6 from 1100 to 1650 kg m<sup>-3</sup> is not sufficient to explain the variability observed for  $\kappa$  for highly soluble materials. Furthermore, the  $\rho_{\text{org}}$  values of carbohydrates and synthetic polymers do not vary significantly yet the variations in  $\kappa$  is significant (cf. Supplement). The implication is that the dominant regulator of CCN activity is  $M_{\text{org}}$  for highly soluble particles.

### 5.3 CCN activity of SOM particles

Isoprene SOM has an O : C ratio of 0.7 and clusters with highly soluble compounds in a van Krevelen diagram (Fig. A2). In agreement, isoprene SOM is observed to activate as a highly soluble particle (King et al., 2010; Engelhart et al., 2011). Smith et al. (2012) found that isoprene SOM forms a homogeneous aqueous phase with ammonium sulfate solution for subsaturated relative humidity, further confirming that isoprene SOM is highly soluble. This result is consistent with the finding of Bertram et al. (2011) that liquid-liquid phase separation (i.e., formation of an insoluble phase) does not occur for highly oxygenated compounds (O : C > 0.7).

By comparison,  $\alpha$ -pinene SOM has a lower O : C ratio of 0.3 to 0.5. It clusters with slightly soluble compounds in a van Krevelen diagram (Fig. A2). One major molecular product is pinonic acid, which is slightly soluble (Yu et al., 1999). Smith et al. (2011) reported that  $\alpha$ -pinene SOM phase separates in the subsaturated regime from aqueous ammonium sulfate, consistent with slightly soluble behavior. The experimental results for the CCN activity of  $\alpha$ -pinene SOM, however, suggest highly soluble particles (VanReken et al., 2005; Hartz et al., 2006; King et al., 2007; Petters et al., 2009b; Frosch et al., 2011; Kuwata et al., 2011). The gap

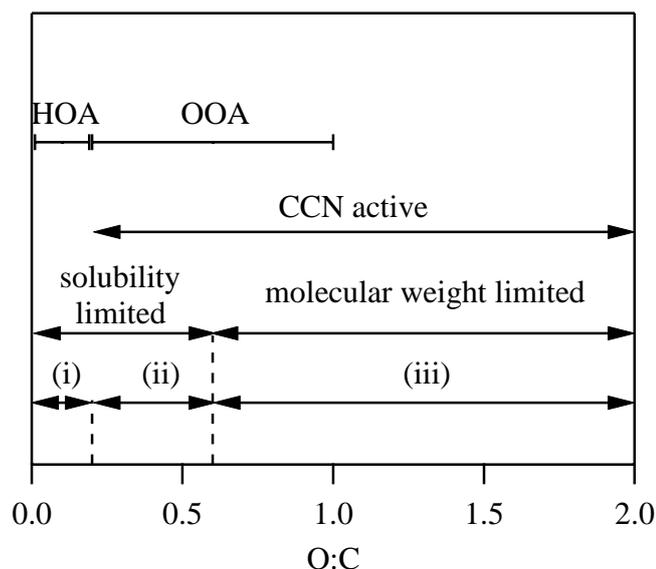
between the understanding of pure compounds and  $\alpha$ -pinene SOM, which is composed of myriad compounds and undergoes continuous water uptake without deliquescence, needs to be investigated in more detail in the future.

The key point might be the absence of the thermodynamic deliquescence limitation. Unlike crystalline particles, amorphous particles, including  $\alpha$ -pinene SOM, continuously uptake water without the first order phase transition, meaning that particles form supersaturated liquid (Varutbangkul et al., 2006; Mikhailov et al., 2009; Kuwata and Martin, 2012b). Liquid adipic acid particles are much more CCN active than solid particles because their activation process is not limited by deliquescence (Bilde and Svenningsson, 2004). A similar phenomenon might occur for  $\alpha$ -pinene SOM. The role of particle phase on water uptake process of SOM particles would need to be investigated further to understand their CCN activation mechanisms.

### 5.4 Atmospheric implications

Ng et al. (2010) compiled observational data of O : C values for the Northern Hemisphere. The results showed that the O : C value of ambient particles can vary from O : C < 0.2, representing hydrocarbon-like organic material (HOA), to O : C > 0.2, representing oxygenated organic material (OOA). Comparison of those O : C values with the results of this study (Fig. 3) suggests, in conformance with expectation, that HOA is insoluble and CCN inactive whereas OOA is CCN active (Fig. 5). This conclusion is supported by the study of Mihara and Mochida (2011), which reported O : C < 0.2 for water-insoluble atmospheric organic material.

Complexity in the chemical composition of organic aerosol particles must also be considered for application of this study's results to the categorization of atmospheric particles. A single particle typically consists of organic material from multiple sources and pathways, possibly influencing the relationship between CCN activity and chemical composition. Statistical data analysis, such as multivariate analysis of mass spectra, can sometimes succeed in characterizing those different types of organic materials



**Fig. 5.** Summary of the relationship between CCN activation mechanism and O:C ratio. Regions representing (i) insoluble, (ii) slightly soluble, and (iii) highly soluble particles are highlighted. The O:C ratios of hydrocarbon-like organic material (HOA) and oxygenated organic material (OOA) are also shown (Ng et al., 2010).

(Zhang et al., 2005; Ulbrich et al., 2009). Such an approach can be expected to be useful for further understanding and categorizing the CCN activity of atmospheric particles.

## 6 Conclusions

The CCN activity of pure organic compounds was investigated to develop a relationship between elemental ratios and CCN activation regimes. The results can serve as a basis for understanding the activation mechanisms of organic mixtures, such as secondary organic material. The experiments were conducted using a homogeneous nucleation particle generator to control the particle phase as a crystalline solid. This generation method was also advantageous for minimizing contamination. The experimental data demonstrated that CCN activation of adipic, suberic, azelaic, and pinonic acids are limited by deliquescence, consistent with the theoretical prediction. Pimelic acid behaved with respect CCN activation as a highly soluble compound, in agreement with reports in literature, though contrary to expectation as a slightly soluble compound.

The experimental results were combined with literature data, including those of dicarboxylic acids, benzoic acids, carbohydrates, fatty acids, and water soluble synthesized polymers. The dependence of  $C$  on O:C was demonstrated, leading to an approach for classifying CCN activation regimes. The effective hygroscopicity parameters  $\kappa$  of pure organic compounds were plotted against O:C ratios,

confirming that activation mechanisms depend on O:C ratios. The simplification of the molecular complexity to an O:C parameter (Eq. 7; Fig. 5) could have high utility for incorporation of chemistry and chemistry feedbacks in larger-scale models, such as coupled climate-chemistry models.

Experimental results for SOM particles were compared with those for pure compounds. Isoprene SOM was clustered with highly soluble compounds in van Krevelen diagram, suggesting that CCN activation was not limited by solubility. This result was consistent with the  $\kappa$  value as well as with formation of uniformly mixed particles at subsaturated regime. On the other hand,  $\alpha$ -pinene SOM was clustered by slightly soluble compounds on the van Krevelen diagram. In agreement, phase separation occurs for mixtures of  $\alpha$ -pinene SOM and ammonium sulfate for subsaturated RH (Smith et al., 2011). For supersaturated RH, however,  $\alpha$ -pinene SOM is highly CCN active. The activation mechanism of  $\alpha$ -pinene SOM has therefore been suggested as highly soluble, even though some  $\alpha$ -pinene oxidation products are slightly soluble. Particle phase as well as complexity in chemical composition may be important because they can remove the thermodynamic limitation of deliquescence for CCN activation. Comparison of these results with literature data on atmospheric organic materials indicate that hydrocarbon-like organic materials (HOA) are insoluble because of their low O:C ratios ( $< 0.2$ ) whereas oxygenated organic materials (OOA) are sufficiently soluble, suggesting the importance of OOA as a water-soluble contributor to atmospheric cloud life cycles.

## Appendix A

### Temperature dependent solubility and $a_{w,D}$ of dicarboxylic acids

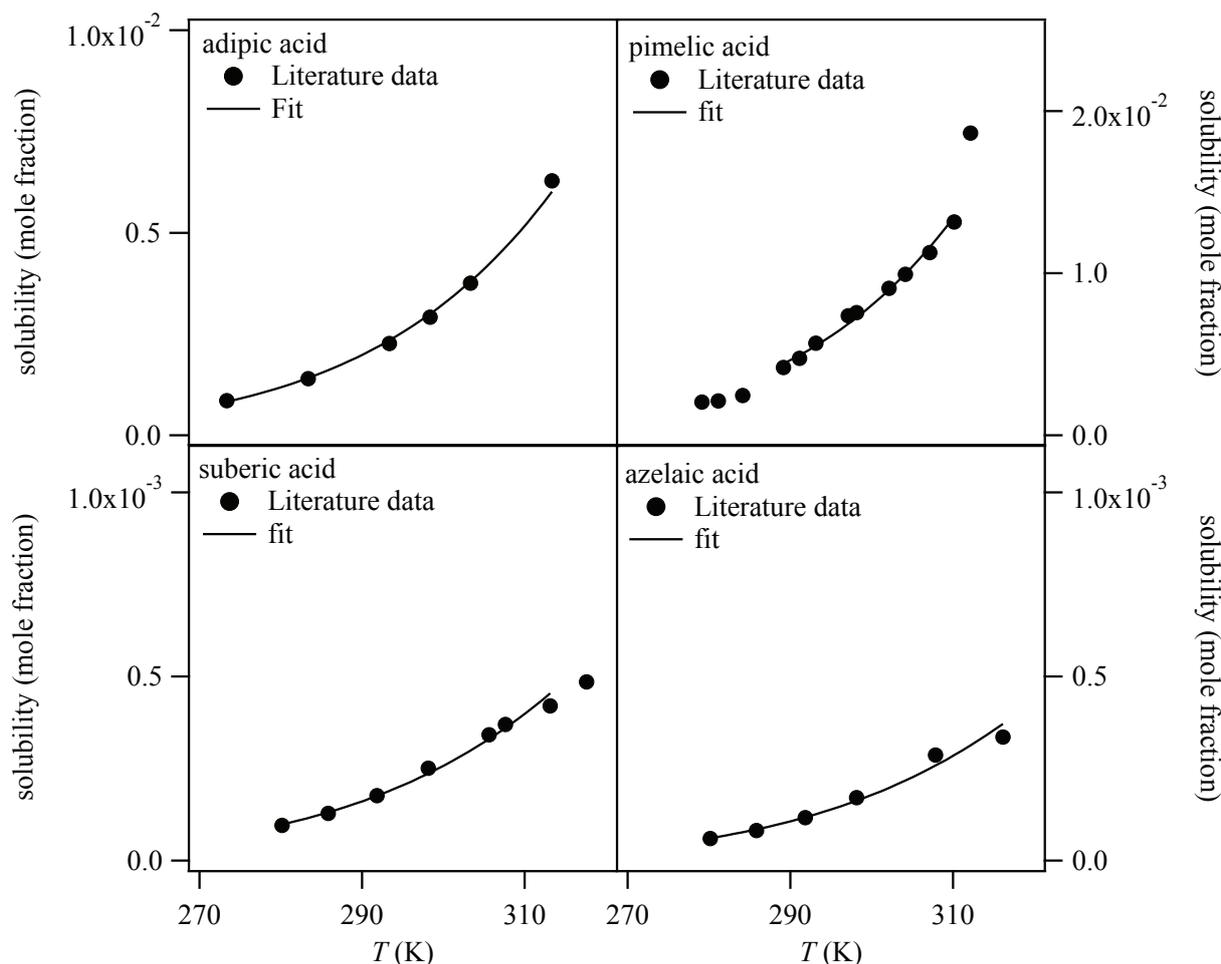
Apelblat and Manzurola (1999) proposed the following equation representing temperature-dependent water solubility of organic acids:

$$\ln(x) = \alpha + \frac{\beta}{T} + \gamma \ln(T) \quad (\text{A1})$$

where  $x$  is solubility in mole fraction, and  $\alpha$ ,  $\beta$ , and  $\gamma$  are empirical parameters obtained by fitting experimental data. This equation was employed to fit literature data, as summarized in Table A1 and Fig. A1. Assuming ideality in solution,  $a_{w,D}$  can be calculated using the following equation (Marcolli et al., 2004)

$$a_{w,D} = \exp(-M_w m_s) = \exp\left(-C \frac{M_w \rho}{M \rho_w}\right) \quad (\text{A2})$$

where  $m_s$  corresponds to molality. This equation is derived from the definition of  $\phi$  for  $\phi = 1$  (Robinson and Stokes, 2002).



**Fig. A1.** Summary of solubility of adipic, pimelic, suberic, and azelaic acids as a function of temperature (Apelblat and Manzurola, 1989; 1990; Gaivoronskii and Granzhan, 2005). The fitting results are also shown (Eq. A1).

**Table A1.** Summary of parameters for the Apelblat-Manzurola equation (Eq. A1).

Compound	$\alpha$	$\beta$	$\gamma$	Temperature range (K)	Data source
Adipic acid	-39.536	-2146.1	7.1825	$273.15 < T < 313.15$	Gaivoronskii and Granzhan (2005)
Pimelic acid	0.99162	-4323.4	1.5065	$289.15 < T < 310.15$	Apelblat and Manzurola (1989)
Suberic acid	15.391	-4530	-1.5003	$280.15 < T < 313.15$	Apelblat and Manzurola (1990)
Azelaic acid	81.422	-7783.7	-11.24	$280.15 < T < 316.15$	Apelblat and Manzurola (1990)

## Appendix B

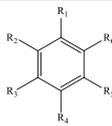
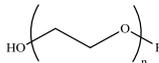
### Van Krevelen diagram

Figure A2 shows the Van Krevelen diagram of the pure compounds as well as that for SOM particles (Heald et al., 2010). Overall, a group of compounds form a cluster on the Van Krevelen diagram. For instance, the elemental ratios for dicarboxylic acids form a line. The relationships between H:C and O:C ratios are examined in Table A2, employing some simplifications. For instance, malic acid ( $C_4H_6O_5$ ) has

a hydroxyl group in between two carboxyl groups, yet this case was not considered in Table A2 to capture the general trends in Fig. A2.

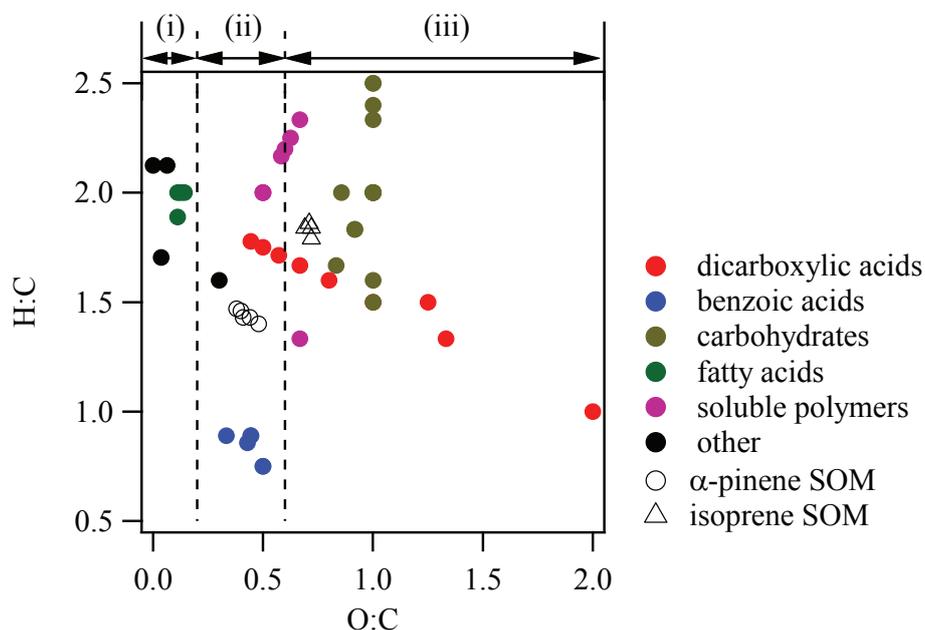
Dicarboxylic acids form a line with a slope of  $-0.5$ . This value is comparable to that reported in Ng et al. (2011) for atmospheric oxygenated organic compounds. H:C ratios of benzoic acids are much lower than those for other compounds, as aromatic carbons increase the denominator for H:C ratios significantly. O:C ratios for carbohydrates are around 1, and H:C ratios are approximately 2. O:C ratios for fatty acids were small due to a long aliphatic

**Table A2.** The positions and functions of each type of compounds on the van Krevelen diagram.  $\nu_C$ , number of carbon atoms;  $\nu_H$ , number of hydrogen atoms;  $\nu_O$  the number of oxygen atoms. The term  $n_{x-R_i}$  denotes the number of atoms  $x$  in  $R_i$ . See Appendix A2 for detail.

	$\nu_C$	$\nu_H$	$\nu_O$	H : C	O : C	Function
 Dicarboxylic acids <sup>a</sup>	$2 + n$	$2 + 2n$	4	$\frac{2+2n}{2+n}$	$\frac{4}{2+n}$	$[H : C] = -\frac{[O : C]}{2} + 2$
 Benzoic acids	$6 + \sum_i n_{C_{R_i}}$	$\sum_i n_{H_{R_i}}$	$\sum_i n_{O_{R_i}}$	$\frac{\sum_i n_{H_{R_i}}}{6 + \sum_i n_{C_{R_i}}}$	$\frac{\sum_i n_{O_{R_i}}}{6 + \sum_i n_{C_{R_i}}}$	$[H : C] = \frac{\sum_i n_{H_{R_i}}}{\sum_i n_{O_{R_i}}} [O : C]$
$C_m(H_2O)_n$ <sup>b</sup> Carbohydrates	$m$	$2n$	$n$	$\frac{2n}{m}$	$\frac{n}{m}$	$[H : C] = 2 [O : C]$
$R-COOH$ Fatty acids	$1 + n_{C-R}$	$1 + n_{H-R}$	2	$\frac{1+n_{H-R}}{1+n_{C-R}}$	$\frac{2}{1+n_{C-R}}$	$[H : C] = \frac{1+n_{H-R}}{2} [O : C]$
 Polyethylene glycol	$2n$	$2 + 4n$	$1 + n$	$\frac{1+2n}{n}$	$\frac{1+n}{2n}$	$[H : C] = 2 [O : C] + 1$

<sup>a</sup> There are exceptions (e.g., malic acid).

<sup>b</sup> There are exceptions (e.g., xylitol.)



**Fig. A2.** Relationships between O : C and H : C ratios of pure compounds and SOM (van Krevelen diagram). The regions (i)–(iii) indicates (i) insoluble, (ii) slightly soluble, and (iii) highly soluble regimes, respectively (see the main text for detail).

chain. H : C ratios for those compounds are also similar to aliphatic compounds. Polyethylene glycol was employed as an example for synthetic polymers (Petters et al., 2009a). H : C ratios of those polymers decrease with the slope of 2, as a dehydration (etherification) mechanism involves

in the formation of those polymers (Heald et al., 2010; Kuwata et al., 2011). Overall, Figure A2 demonstrates that a van Krevelen diagram is useful in classifying atmospheric relevant pure compounds.

Supplementary material related to this article is available online at: <http://www.atmos-chem-phys.net/13/5309/2013/acp-13-5309-2013-supplement.pdf>.

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