

## Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review

Jiming Sun, Parisa A. Ariya

### Abstract

Organic substances have been recognized as active cloud condensation and ice formation nuclei for several decades. In some regions of the world, these organic compounds (OC) consist predominantly of suspended matter mass, which can have local (e.g. toxicity, health hazards) and global (e.g. climate change) impacts. However, due to the complexity of their chemical nature, the significance of organic molecules in driving physical and chemical atmospheric processes is still very uncertain and poorly understood. The aim of this review paper is to assess the current state of knowledge regarding the role of organic aerosols (including bioaerosols) as cloud condensation nuclei (CCN), as well as to compare the existing theoretical and experimental data. It seems that classical Kohler theory does not adequately describe the hygroscopic behaviour of predominantly identified organic CCN such as pure dicarboxylic acid particles. Factors such as surface tension, impurities, volatility, morphology, contact angle, deliquescence, and the oxidation process should be considered in the theoretical prediction of the CCN ability of OC and the interpretation of experimental results. Major identified constituents of organic CCN, their main sources and their CCN properties will be herein reviewed. We will also discuss areas of uncertainty and expose key issues deserving of future research.

### 1. Introduction

Airborne particles, aerosols, are recognized as important players in climatic processes through interactions with radiation. Aerosols also lead to the formation of cloud droplets and ice crystals by serving as cloud condensation nuclei (CCN) and ice nuclei (IN). CCN are particles that in the presence of supersaturated water vapour (Seinfeld and Pandis, 1998) activate to become cloud and fog droplets. Ice particles are mainly formed through heterogeneous nucleation by several mechanisms (e.g., deposition, condensation freezing, immersion and contact) which require the presence of IN. Clouds play a key role in the Earth's radiation budget through absorption of terrestrial infrared radiation and reflection of solar irradiation. However, minute variations in cloud albedo may significantly modify the planetary albedo and thus affect the global climate (Lee et al., 1997; Stephens et al., 1990). Cloud albedo depends upon droplet size distributions (Twomey, 1977) and hence, any perturbations in the population of CCN can have a significant impact on the optical properties of the clouds. Aerosols affect the lifetime of clouds, size distributions of cloud droplets, glaciation rates and the distribution of water mass in different atmospheric layers (Hudson, 1992; Lohmann and Lesins, 2002). The Intergovernmental Panel on Climate Change (Intergovernmental Panel on Climate Change, 2001) has highlighted the aerosol-cloud-climate relationship as one of the least well understood. The spatial distribution of CCN and IN and the dependence of their efficiency on the size distribution, chemical structure and chemical composition of the aerosol population are key issues that need to be addressed prior to understanding the links between aerosols, clouds and ultimately, climate.

Carbonaceous aerosols are a significant subgroup of atmospheric aerosols, which consist of elemental carbon (EC) (black/graphitic carbon) and organic carbon. The latter is a complex mixture of hundreds of organic compounds (OC) (e.g., Graedel et al., 1986) and is the focus of the present review. During their residence time in the troposphere, which varies from days to weeks (Seinfeld and Pandis, 1998), aerosols can undergo chemical transformations and are removed from the atmosphere by deposition at the surface (dry deposition) or by incorporation into precipitating particles (wet deposition). Fig. 1 is a simplified schematic of organic aerosol transformation in the atmosphere. Most atmospheric aerosols tend to have a mixed chemical composition, including a variety of inorganic and organic species. Organic particulate matter can represent as a complex mixture of OC either of biogenic or non-biogenic origin (Andrews et al., 1997; Masclat and Hoyau, 1995; Saxena and Hildemann, 1996; White, 1990). Recent studies on atmospheric aerosols have shown that organic aerosols are an important part of the global CCN budget. Their activation capability is assumed to be comparable to that of sulfate aerosols, which are considered the most effective CCN (Acker et al., 2002; Matsumoto et al., 1997). Several mono-carboxylic acids (MCA) and dicarboxylic acids (DCA) have been identified as the predominant constituents of organic CCN (Yu, 2000). Some researchers have suggested that humic-like substances (HULIS) may also have an impact on the hygroscopicity of aerosols and the formation of CCN (Facchini et al., 1999b; Charlson et al., 2001). The activation capability of some pure OC as CCN has been also experimentally evaluated (Corrigan and Novakov, 1999; Cruz and Pandis, 1997; Hori et al., 1990; Kumar et al., 2003; Prenni et al., 2001; Raymond and Pandis, 2002; Giebl et al., 2002). However, the CCN capability for most groups of OC has yet to be examined and their hygroscopic growth mechanism is not fully understood.

There are several excellent review articles and books on the measurement of organic aerosols, their interactions with radiation, the toxicology of bioaerosols, heterogeneous ice nucleation, constituents of CCN, as well as chemical transformation of organic films and comprehensive chemical and physical properties of organic aerosols (e.g., Graedel et

al., 1986; Stephens et al., 1990; Vali, 1985, 1995; Vali et al., 1976; Szyrmer and Zawadzki, 1997; Seinfeld and Pandis, 1998; Hudson, 1992; Yu, 2000; Jacobson et al., 2000; Hurst et al., 2002; Rudich, 2003; Kanakidou et al., 2004). For this reason, we herein focus on the current state of science regarding (a) the possible sources of organic CCN including the primary and secondary OC, (b) the role of organic aerosols (including bioaerosols) acting as CCN in the atmosphere, (c) theoretical and experimental knowledge of their activation processes as well a newly discovered chemical reactions/modifications induced by bioaerosols in the atmosphere. We will also promote future research by identifying some critical knowledge gaps in this novel domain.

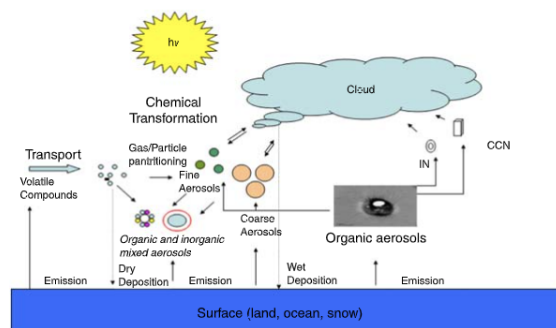


Fig. 1. The simplified schematic of organic aerosol transformation in atmosphere.

## 2. OC as CCN

The origin and nature of CCN has become a central issue in climate change due to their strong ability to modulate cloud microstructure and hence, radiative properties (Charlson et al., 1987). The CCN in the atmosphere has been found to include water-soluble compounds (Hobbs et al., 1974). As well, a large fraction of organic mass includes water-soluble species. For instance, 40% of the total carbon in Denver (Cadle and Groblicki, 1982), 20–50% in the polluted Po Valley (Zappoli et al., 1999), 80% at a background site of Aspöreten (Central Sweden), and 50–70% of the total worldwide organic carbon include water-soluble polar OC (Sempere and Kawamura, 1994). Several groups of OC have strong polarity, surface activity, solubility and affinity for water (Keene and Galloway, 1988). Chemical characterization of atmospheric aerosols has revealed OC among the major constituents of fine aerosols (0.01–1  $\mu\text{m}$ ), and their concentration is comparable to that of sulfate around the globe (Heintzenberg, 1989; Novakov and Penner, 1993; Saxena and Hildemann, 1996). Although the size distribution and composition of organics differ spatially and temporally, organic aerosols constitute an important fraction of fine aerosols. For instance, fine-mode organic aerosols make up to 80% of the wet-season aerosol mass in the Amazon Basin (Artaxo and Hansson, 1995; Wouters et al., 1993).

During field studies scientists first noted the importance of organics as CCN; the concentration of water-soluble organics has, in fact, been positively correlated with the number of CCN. Observations made by Desalmand et al. (1985) have shown that vegetation can produce CCN and Novakov and Penner (1993) indicated that 37% of the CCN number-concentration measured at a marine site could be accounted for using total sulfate particles, while the remaining 63% were attributed to organic aerosols. Hegg et al. (1995) confirmed that most CCN over the northeastern Atlantic coast of the United States are not sulfate particles. Hitznerberger et al. (1999) investigated the contribution of organic material to the CCN aerosols in Europe urban aerosols in Vienna, finding it to be 48% of the total mass concentration of CCN at a supersaturation ratio of 0.5%. Moreover, organic materials were detected in cloud water (Khwaja et al., 1995; Limbeck and Puxbaum, 2000; Loflund et al., 2002) in surprisingly high concentrations, relative to the inorganic ions, but this observation does not indicate that all of these OC could act as CCN. It is of note that Saxena et al. (1995) observed that organics could enhance water absorption of in OC at a remote location (Grand Canyon), hinting at the fact that organics may not only act as CCN, but also increase the nucleating ability of inOC. Therefore, determining the OC that may act as CCN and their influence on sulfates in the formation of CCN is the focus of much recent research.

Recent thermal analysis studies on the composition of CCN have suggested that anthropogenic organic materials contribute considerably to the number of CCN (Ishizaka and Adhikari, 2003). Matsumoto et al. (1997) described a significant correlation between total water-soluble organic salt (formate, acetate, oxalate and methanesulfonate (MSA)) and CCN concentrations at 1.0% and 0.5% supersaturation ratios. Several MCA and DCA have also been identified as predominant constituents of organic CCN (Yu, 2000). Recently some researchers noted that HULIS might have an impact on the hygroscopicity of aerosols and the formation of CCN (Facchini et al., 1999b; Charlson et al., 2001). Interestingly, it has been shown that some bacteria serve as CCN (Bauer et al., 2003; Franc and DeMott, 1998) and have indeed been observed in the active form in clouds (Sattler et al., 2001). OC (including bioaerosols) acting as CCN will

be discussed in more detail in the following sections.

### 2.1. *Hygroscopicity of HULIS*

Recently, it has been recognized that HULIS consisting primarily of polysaccharide and aliphatic substructures are major components of continental organic aerosols and can indeed be of biogenic origin. HULIS comprise 20–50% of water-soluble organic aerosols collected in urban (Havers et al., 1998a), rural (Kiss et al., 2002) and high Alpine environments (Krivacsy et al., 2001), as well as in Amazonia (Mayol-Bracero et al., 2002) and fog samples (Krivacsy et al., 2000; Kiss et al., 2001). Kiss et al. (2003) estimated the average molecular weight of these substances range from 215 to 345 Da (1 Da = 1 g mol<sup>-1</sup>).

The origin of these atmospheric macromolecular substances was first attributed to agricultural burning (Mukai and Ambe, 1986; Facchini et al., 1999a). However, recently Decesari et al. (2002) demonstrated that the atmospheric oxidation of soot could produce HULIS in aerosols. They concluded that the CCN effectiveness of soot aerosols likely had its origin in these oxidation processes. Limbeck et al. (2003) have suggested the formation of HULIS may be via a heterogeneous reaction of gaseous isoprene on acidic particles in the atmosphere. HULIS were identified in fine particles and exhibit good water solubility (Zappoli et al., 1999).

Facchini et al. (2000) investigated the surface-active behaviour of polycarboxylic acids, whose molecular structure is analogous to that of HULIS, and found their more effective surface-active species compares with neutral compounds, mono- and DCA in wet aerosols, as well as cloud and fog samples. They concluded that HULIS has a greater surface tension decrease compared to that of pure water. Surface tension modifications of cloud droplets due to HULIS may thus have important impacts on cloud microphysical properties. Moreover, this kind of organic matter has also been identified in fog droplets with a scavenging ratio similar to that of inorganic ions (Facchini et al., 1999b; Krivacsy et al., 2000; Kiss et al., 2001). On the basis of these observations, it can be concluded that HULIS should serve as active CCN. However, to our knowledge, detailed experiments on the activation capacity of these compounds have yet to be performed.

### 2.2. *MCA and DCA acting as CCN*

Among the observed OC, ion chromatography (IC) analysis has shown that the most frequently observed organic species in the condensed phase in the atmosphere are low molecular weight MCA and DCA, with MCA much more abundant than DCA (Keene and Galloway, 1988; Yu et al., 1991a, b). Amongst MCA, formic and acetic acids are the dominant observed species in the gas phase (Dawson et al., 1980; Yu et al., 1990), as well as in aerosols (Andreae et al., 1988a, b, Alvarez et al., 199b), precipitation (Keene and Galloway, 1988; Yu et al., 1991a, b), and cloud and fog water (Weathers et al., 1986). Formate and acetate concentrations in the aerosol phase have been observed to vary from 0.02 to 5.3 nmol m<sup>-3</sup> and from 0.03 to 12.4 nmol m<sup>-3</sup>, respectively. In all, 34–77% of formate aerosols and 21–66% of acetate aerosols are present in fine aerosols (Yu, 2000). Note that the concentrations of formic and acetic acids in the gas phase range from 0.8 to 612 nmol m<sup>-3</sup> and 1.2 to 653 nmol m<sup>-3</sup>, respectively (Yu, 2000). Hence, despite the fact that most (98–99%) of these two volatile organic acids are present in the gas phase, their concentrations in aerosol particles are sufficient to make them good candidates as CCN (Yu, 2000). Other organic acids emitted from vegetation and biomass burning have also been suggested as important contributors to CCN (Yu, 2000).

Since the vapour pressure of DCA is lower than that of corresponding MCA by a factor of  $10^2$ – $10^4$  (Ludwig and Klemm, 1988), DCA dominate in aerosol particles and constitute only a small fraction of the total particulate water-soluble OC in the atmosphere. For example, Rogge et al. (1993) indicated that water-soluble DCA, readily present in the aerosol phase, account for approximately 2–4% of total organic aerosol mass. Numerous studies

Table 1  
Literature data of dicarboxylic acids in aerosol samples ( $\text{ng m}^{-3}$ )

| Location     | Location   | Oxalic     | Glyoxalic | Malonic   | Pyruvic  | Succinic | Glutamic  | Adipic   | Phthalic | Literature                   |
|--------------|------------|------------|-----------|-----------|----------|----------|-----------|----------|----------|------------------------------|
| Los Angeles  | Urban      | —          | —         | 33        | —        | 66       | 32        | 14       | 60       | Rogge et al. (1993)          |
| Tokyo        | Urban      | 1352       | 174       | 322       | 27       | 279      | 81        | 31       | 135      | Sempere and Kawamura (1994)  |
| New York     | Semiurban  | 58–360     | 26–68     | 43–107    | 41–103   | 55–167   | —         | —        | —        | Khawaja (1995)               |
| Antarctica   | Background | 3.1        | 0.3       | 0.4       | 0.2      | 5.8      | 0.6       | 0.9      | 1.7      | Kawamura et al. (1996a, b)   |
| Vienna       | Urban      | 340        | 22        | 244       | 62.5     | 117      | 26.0      | 117      | 18       | Limbeck and Puxbaum (1999)   |
| Sonnblick    | Background | 153        | 9.6       | 22        | 2.6      | 14       | 2.7       | 4.4      | 3.3      | Limbeck and Puxbaum (1999)   |
| South Africa | Background | 193        | 38        | 142       | < 1      | 58       | 8.8       | 7.9      | 3.3      | Limbeck and Puxbaum (1999)   |
| Nanjing      | Urban      | 178–1423   | —         | 26.9–177  | —        | 28.9–293 | 15.8–95.1 | 7.5–102  | —        | Wang et al. (2002)           |
| Las Vegas    | Urban      | 800 (max)  | —         | 120 (max) | —        | 42 (max) | —         | —        | —        | Tran et al. (1998)           |
| Alert        | Arctic     | 13.2–40.9  | —         | 3.2–11.6  | —        | 2.3–15.4 | 0.8–2.2   | 0.2–6.8  | —        | Narukawa et al. (2002)       |
| Syowa        | Antarctic  | 1.6–10.3   | —         | 0.1–2.7   | —        | 0.6–61.5 | 0.3–2.3   | 0.5–1.8  | 0.9–2.6  | Kawamura et al. (1996a, b)   |
| Takasaka     | Mountain   | 5.1        | —         | 12.0      | —        | 25.0     | 10.1      | 5.2      | 22.1     | Satsumabayashi et al. (1990) |
| Karuizawa    | Mountain   | 3.9        | —         | 11.1      | —        | 21.5     | 0.7       | 4.7      | 19.5     | Satsumabayashi et al. (1990) |
| California   | Aircraft   | 8.0–59     | —         | 4.0–44.0  | —        | 0.0–24   | —         | —        | —        | Hegg et al. (2002)           |
| South Africa | Background | 14.8–179.5 | 0.9–21.5  | 3.0–227.8 | 0.9–19.9 | 4.8–31.1 | 0.7–4.0   | 0.6–15.9 | 0.2–6.6  | Limbeck et al. (2001)        |

have shown that the most abundant DCA is oxalic acid ( $C_2$ ), followed by malonic ( $C_3$ ) and succinic acid ( $C_4$ ), and their concentrations are greater in polluted cities than in remote or marine locations (Kawamura et al., 1995, 1996a, b; Kerminen, 2001; Kerminen et al., 2000; Sempere and Kawamura, 1996) (Table 1).

In earlier studies, OC, in addition to acting as solute in vapour-pressure depression, have often been considered players in delaying droplet formation (Bigg, 1986) or droplet evaporation (Gill et al., 1983). Such effects have long been attributed to organic films or coatings on incipient cloud droplets. Recent studies have paid particular attention to the oxidation processes of organic films and the cloud condensation activity of organic aerosols. In addition, much research is under way to shed light on the mechanism of hygroscopic growth for these OC (Table 2). In part 4, we will outline and compare existing experimental and theoretical studies.

### 2.3. Cloud-condensation-nucleating activity of bacteria

Bacteria ( $\approx 0.25$ – $8 \mu\text{m}$  in diameter) are a group of very metabolically diverse, prokaryotic, unicellular microorganisms, usually possessing cell walls. They are water-parasitic, saprophytic on plants and animals, or found in soil. Different types of bacteria can be classified by Gram-staining (Holt et al., 1994). Gram-staining reveals cell shape and size and separates bacteria into two groups based on the structure and chemistry of their cell envelopes (Chapin, 1995): Gram-positive bacteria (GPB) appear blue or purple after staining and Gram-negative bacteria (GNB) appear pink or red. Bacteria have been observed in the boundary layer, in the upper troposphere (Lindemann et al., 1982; Lindemann and Uppel, 1985), and even in the stratosphere at altitudes up to 41 km above sea surface (Wainwright et al., 2003). The flux of bacteria entering the atmosphere is recognized as originating from two types of temperate vegetation zones: (a) high primary production row crop area, and (b) relatively low-production desert area. The highest flux measured was  $1.95 \times 10^6$  colony forming units (CFU)  $\text{m}^{-2}\text{h}^{-1}$  for the crop area (Lindemann et al., 1982) and  $1.7 \times 10^3$  CFU  $\text{m}^{-2}\text{h}^{-1}$  for the desert area (Lighthart and Sharffer, 1994). The concentration of bacteria in the atmosphere depends on transport from the surface boundary layer. The bacteria flux is closely connected to the reproduction rate of bacteria. Neglecting death and other losses, the higher the amount of primary production (which coincides with bacterial nutrient production), the more bacteria is generated and available for release into the atmosphere.

With the flux of bacteria from plant surfaces and soil into the air, living and dead bacteria, including ice-nucleating species, have been found in clouds and fog (Fuzzi et al., 1997), raindrops (Maki and Willoughby, 1978; Parker, 1968) and hailstones (Mandrioli et al., 1973). Bauer et al. (2002) have shown that average mass concentrations of bacteria amounted to 0.01% of OC in cloud water, snow, rain and aerosol samples. Although the mass concentrations of bacteria were low compared with other organic aerosols, the concentrations of the bioorganic cells ( $10^3$ – $10^4$  cells  $\text{m}^{-3}$ ) were relatively high and of the same order of magnitude as IN (Bauer et al., 2002; Sattler et al., 2001).

Bacteria have also been identified as effective IN (e.g.; Soulage, 1957; Maki et al., 1974; Schnell, 1976;

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<https://www.sciencedirect.com/science/article/pii/S135223100500498X>

Vali et al., 1976; Sands et al., 1992) and some studies found certain species of active ice-nucleating bacteria at altitudes up to 6 km (Lindemann et al., 1982; Lindemann and Upper, 1985). The cloud condensation ability of bacteria has also been considered. Tranc and Demott (1998) observed that several strains of plant pathogenic bacteria, *Erwinia carotovora* and *E. carotovora atroseptica*, are active CCN (25–30% of the aerosolized bacteria cells at 1% water supersaturation ratio). They proposed that significant numbers of tested bacterial strains are actively involved in atmospheric cloud formation and precipitation processes following natural aerosolization and vertical transport to cloud level. Bauer et al. (2003) have shown that both Gram-positive and -negative bacteria (*Micrococcus agilis*, *Mycoplana bullata*, and *Brevundimonas diminuta*) are activated as CCN at supersaturations between 0.07% and 0.11%. They suggested that the chemical composition, structure and hydrophilicity of the outer cell surface layer of bacteria could play important roles in CCN activity. Measurements of water contact angle on hundreds of bacteria (Sharma and Rao, 1999) demonstrated that, in some cases, the contact angle of water is very low (less than 161), indicating that some bacteria are seemingly very hydrophilic.

There is a slight variation in the number concentration of bacteria in clouds with altitude and location. At Mt. Sonnblick (3106 m above sea level (a.s.l.), Austria) during spring 1997, the average number of bacteria in cloud water was about  $1500 \text{ mL}^{-1}$  (Sattler et al., 2001). At Mt. Rax (1644 m.a.s.l., Austria) during spring 1999 and 2000, the average bacteria in cloud water was  $2.0 \times 10^4 \text{ cells mL}^{-1}$ , while the air equivalent concentration of bacteria in clouds was estimated to be  $5.9 \times 10^3 \text{ cells m}^{-3}$  (Bauer et al., 2002). This value is significantly smaller than the average number of cloud droplets per given unit volume ( $2 \times 10^8 \text{ m}^{-3}$ ), and also lower than the concentration of CCN in clouds ( $(1.0\text{--}2.0) \times 10^8 \text{ m}^{-3}$ ), at supersaturation of 0.28% (Ross et al., 2003). Sattler et al. (2001) suggested that bacteria are not an important source of CCN, and their mass corresponds to only 0.01% of the organic carbon. This value was obtained using a conversion factor of  $17 \text{ fg C cell}^{-1}$  for the carbon content of bacteria, a typical value for bacteria in marine and freshwater ecosystems (Sattler et al., 2001), and an average mass concentration of bacteria of  $0.34 \text{ ng C mL}^{-1}$  (Bauer et al., 2002). However, a very recent study shows the cellular (protein-containing) particles are a major fraction of atmospheric aerosols with roughly  $1000 \text{ Tg yr}^{-1}$  compared with  $3300 \text{ Tg yr}^{-1}$  for sea salt and  $2000 \text{ Tg yr}^{-1}$  for mineral dust (Jaenicke, 2005). Due to the lack of understanding regarding the physical and chemical processes for bioaerosol CCN formation, this domain of research deserves further study before drawing any definite conclusions. It is also noteworthy that besides bacteria, the roles of other types of bioaerosols (large molecules or volatile compounds, live or dead, that are remnants of biological activities, e.g., pollen, viruses, fungi) as effective CCN have yet to be fully understood.

Table 2  
 Chemical properties of investigated compounds and experimental results

| Compound      | Formula  | Molecular weight | Solubility in water (mg L <sup>-1</sup> )     | Density (g cm <sup>-3</sup> ) | Vapour pressure <sup>a</sup> (mmHg) | Contact angle with H <sub>2</sub> O <sup>b</sup> | D <sub>50</sub> <sup>c</sup> (nm)        |
|---------------|--|------------------|---|-------------------------------|-------------------------------------|--|--|
| Oxalic acid   | C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>   | 90.03            | 2.2 × 10 <sup>5d</sup>                        | 1.900 <sup>e</sup>            | 3.5 × 10 <sup>-5</sup>              | —  | —  |
| Malonic acid  | C <sub>3</sub> H <sub>4</sub> O <sub>4</sub>   | 104.06           | 7.6 × 10 <sup>5d</sup>                        | 1.631 <sup>f</sup>            | 1.0 × 10 <sup>-5</sup>              | —  | —  |
| Succinic acid | C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>   | 118.09           | 8.3 × 10 <sup>4d</sup>                        | 1.572 <sup>f</sup>            | 6.9 × 10 <sup>-7</sup>              | —  | —  |
| Glutaric acid | C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>   | 132.12           | 1.6 × 10 <sup>6d</sup>                        | 1.424 <sup>f</sup>            | 4.1 × 10 <sup>-6</sup>              | 0°   | 44 ± 7 <sup>b</sup> , 60 <sup>f</sup>    |
| Adipic acid   | C <sub>6</sub> H <sub>10</sub> O <sub>4</sub>  | 146.14           | 3.4 × 10 <sup>4f</sup>                        | 1.360 <sup>f</sup>            | 1.5 × 10 <sup>-7</sup>              | 0°   | 107 ± 18 <sup>b</sup> , 100 <sup>a</sup> |
| Malic acid    | C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>   | 139.09           | 9.0 × 10 <sup>5f</sup>                        | 1.595 <sup>f</sup>            | 3.3 × 10 <sup>-8</sup>              | —  | 52 <sup>f</sup>                          |
| Phthalic acid | C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>   | 166.13           | 9.6 × 10 <sup>3f</sup>                        | 1.593 <sup>f</sup>            | —                                   | —  | —  |
| Oleic acid    | C <sub>18</sub> H <sub>34</sub> O <sub>2</sub> | 282.50           | Very low <sup>e</sup>                         | 0.890 <sup>g</sup>            | —                                   | —  | —  |
| Stearic acid  | C <sub>18</sub> H <sub>36</sub> O <sub>2</sub> | 284.50           | Very low <sup>e</sup>                         | 0.94 <sup>g</sup>             | —                                   | —  | —  |
| Colesterol    | C <sub>27</sub> H <sub>46</sub> O              | 386.66           | < 2.0 × 10 <sup>1b</sup>                      | 1.067 <sup>b</sup>            | —                                   | 0°   | 48 ± 8 <sup>b</sup>                      |
| Glutamic acid | C <sub>5</sub> H <sub>9</sub> NO <sub>4</sub>  | 147.13           | 6.6 × 10 <sup>3</sup> –7.3 × 10 <sup>3b</sup> | 1.538 <sup>b</sup>            | —                                   | —  | 38 ± 6 <sup>b</sup>                      |
| Hexadecane    | C <sub>16</sub> H <sub>34</sub>                | 226.45           | 9.0 × 10 <sup>-4b</sup>                       | 0.773 <sup>b</sup>            | —                                   | > 90°  | > 200 <sup>b</sup>                       |
| Hexadecanol   | C <sub>16</sub> H <sub>34</sub> O              | 242.45           | 3.0 × 10 <sup>-2b</sup>                       | 0.830 <sup>b</sup>            | —                                   | 45°  | > 200 <sup>b</sup>                       |
| Leucine       | C <sub>16</sub> H <sub>13</sub> O <sub>2</sub> | 131.17           | 8.8 × 10 <sup>3</sup> –9.7 × 10 <sup>3b</sup> | 1.239 <sup>b</sup>            | —                                   | > 90°  | > 200 ± 34 <sup>b</sup>                  |
| Myristic acid | C <sub>14</sub> H <sub>28</sub> O <sub>2</sub> | 228.38           | < 2.0 × 10 <sup>1b</sup>                      | 0.866 <sup>b</sup>            | —                                   | > 90°  | > 200 <sup>b</sup>                       |
| Norpinic acid | C <sub>8</sub> H <sub>12</sub> O <sub>4</sub>  | 172.18           | 4.7 × 10 <sup>4b</sup>                        | 0.800 <sup>b</sup>            | —                                   | —  | 42 ± 7 <sup>b</sup>                      |
| Palmitic acid | C <sub>8</sub> H <sub>32</sub> O <sub>2</sub>  | 256.43           | 7.0 <sup>b</sup>                              | 0.853 <sup>b</sup>            | —                                   | > 90°  | > 200 <sup>b</sup>                       |
| Pinic acid    | C <sub>9</sub> H <sub>14</sub> O <sub>4</sub>  | 186.21           | > 8.46 × 10 <sup>4b</sup>                     | 0.800 <sup>b</sup>            | —                                   | —  | 38 ± 6 <sup>b</sup>                      |
| Pinonic acid  | C <sub>10</sub> H <sub>16</sub> O <sub>3</sub> | 184.24           | 6.4 × 10 <sup>3</sup> –7.1 × 10 <sup>3b</sup> | 0.786 <sup>b</sup>            | —                                   | 0°   | 50 ± 9 <sup>b</sup>                      |

<sup>a</sup>Prenni et al. (2001) at 30 °C.

<sup>b</sup>Raymond and Pandis (2002).

<sup>c</sup>Dry diameter at 50% activation under supersaturation 1%.

<sup>d</sup>Howard and Meylan (1997).

<sup>e</sup>Kumar et al. (2003).

<sup>f</sup>Hori et al. (2003).

<sup>g</sup>Cruz and Pandis (1997).

### 3. Sources of organic CCN

Organic CCN can come from primary organic aerosols (POA) and secondary organic aerosols (SOA). Both are known to contribute significantly to the atmospheric population of CCN. In this section, we summarize actual knowledge on the possible sources for the primary organic CCN, the chemical reactions responsible for the formation of secondary organic CCN, as well as the effects of oxidation of the organic coatings on the improvement of CCN ability of atmospheric aerosols.

#### 3.1. Primary organic CCN

The presence of primary OC in atmospheric particles originates from a wide range of primary emissions of anthropogenic and biogenic activities, as well as the burning of open biomass due to natural fires and land-use practices. The main primary OC can be attributed to both combustion and biogenic emission.

The combustion emissions mainly come from vehicular exhaust and biomass burning. Based on energy statistics for the year 1996, Bond et al. (2004) estimated emissions of primary organic carbon are 2.4, 5.8, 25 Tg yr<sup>-1</sup> from the combustion of fossil fuels, combustion of biofuels and open biomass burning, respectively.

Vehicular exhaust is the main pathway of the anthropogenic emissions and is the primary source of DCA and MCA. The dominant DCA in atmospheric particles are oxalic acid (C<sub>2</sub>), followed by malonic acid (C<sub>3</sub>) and succinic acid (C<sub>4</sub>) atmospheric particles (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Saxena et al., 1995; Yao et al., 2003). In particular, relatively low C<sub>3</sub>/C<sub>4</sub> mass ratios have been found to be associated with the overwhelming contributions to these acids from vehicular exhaust in some studies (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Wang et al., 2002). They also found ratios larger than unity concurrent with elevated concentrations of oxidants and attributed the source of DCA to secondary atmospheric reactions. From this view, Yao et al. (2004) suggested the DCA were mainly attributed to vehicular emissions in the winter and secondary sources in the summer.

Furthermore, some of MCA also may come from the primary sources. At present, most measurement techniques cannot discriminate between the organic aerosols formed from primary emissions and those from secondary formation. Souza et al. (1999) have shown vehicular emissions appeared to be the primary source of acetic acid during the daytime.

Biomass-burning studies have spawned many papers on the physical, chemical, and thermodynamic properties of biomass-burning particles. Reid et al. (2004) recently reviewed the physical properties of biomass-burning particles. The smoke particle properties are well described in their paper. Around 80–90% of the volume of smoke particle is in the accumulation mode ( $d_p < 1 \mu\text{m}$ ). Smoke particles are composed of ~60% organic carbon and ~5–10% black carbon (BC). It has also been known for decades that smoke particles can be very effective CCN at supersaturations greater than 0.5%. However, the fresh smoke particles have been shown to have relatively small hygroscopicity. The primary organic acids such as oxalate, formate, acetate constitute less than 1% of particle mass, while in aged plumes each of these species can increase up to 3% of mass. However, recently while collecting the smoke aerosols directly over the fire-mass concentration, Gao et al. (2003) found high concentrations of such primary OC as: acetate ( $830 \text{ ng m}^{-3}$ ), formate ( $380 \text{ ng m}^{-3}$ ), oxalate ( $750 \text{ ng m}^{-3}$ ), glutarate ( $300 \text{ ng m}^{-3}$ ), succinate ( $470 \text{ ng m}^{-3}$ ) and malonate ( $1200 \text{ ng m}^{-3}$ ). Falkovich et al. (2004) have also shown high concentration of primary dicarboxylic particles in biomass burning. Therefore, biomass burning is also a source of primary organic CCN.

Biosphere is a major source for primary biogenic organic aerosols. Primary biogenic organic aerosols include whole organisms (e.g. bacteria, fungi) and reproductive material (e.g. pollen), fragments (e.g. plant waxes), decaying organic matter, and surfactants generated in the sea by bubble-bursting processes. Penner et al. (2001) estimated the global biogenic emission of primary carbonaceous aerosols was about  $56 \text{ Tg yr}^{-1}$  ( $> 1 \mu\text{m}$  in size) for the year 2000.

In recent field measurement over the North Atlantic Ocean, O'Dowd et al. (2004) found marine aerosols contribute significantly to the global aerosol load. The organic mass fraction contributes 63% to the submicrometre marine aerosols (about 45% is water-insoluble and about 18% water-soluble) during plankton blooms progressing from spring through to autumn. Detailed analysis revealed the water-soluble organic aerosols are mainly comprised of aliphatic and HULIS, and only a small amount of oxidized species (Cavalli et al., 2004). This primary biogenic organic source enriches marine aerosol particles, particularly the fine-aerosol fraction in the oceanic surface layer, and is transferred to the atmosphere by bubble-bursting processes. Therefore, in view of these wide biological activities, Jaenicke (2005) estimated that the primary biogenic emission, including both marine and continental biospherical sources, is presently approximately  $1000 \text{ Tg yr}^{-1}$ . This important source of biogenic organic CCN from the ocean is omitted from current cloud research and should be taken into account.

### 3.2. Secondary organic CCN

Secondary organic CCN consist mainly of those from secondary biogenic aerosols, secondary anthropogenic organic aerosols and the oxidation products of soot. Herein we discuss only the oxidation products of biogenic volatile organic compounds (BVOCs) and soot. In the next section, we will discuss the secondary anthropogenic organic aerosols and the impact of organic films.

#### 3.2.1. Secondary biogenic CCN

Secondary biogenic organic aerosols are formed from oxidation of volatile organic compounds (VOC) emitted from biological organisms. Biogenic emissions are driven by temperature, light and vegetation. The new estimation of biogenic VOC is between  $756$  and  $810 \text{ Tg C yr}^{-1}$ , which is about 5.5 times higher than the anthropogenic VOC emissions (Tsigaridis et al., 2005). The predominant precursor species of biogenic SOA mass production are monoterpenes ( $\text{C}_{10}\text{H}_{16}$ ) (78%), followed by sesquiterpenes (22%) (Chung and Seinfeld, 2002). Recent observations indicate the global terpene emission is possibly larger than previously estimated (Holzinger et al., 2004). Therefore, monoterpenes appear to be the major precursors of secondary organic particulate matter from BVOCs. Among the types of monoterpenes,  $\alpha$ -pinene (endocyclic double bond),  $\beta$ -pinene (exocyclic double bond), sabinene and limonene account for 40–80% of the overall terpene emission on a global scale (Kanakidou et al., 2004).

VanReken et al. (2005) recently have shown the CCN ability of the reaction results from ozone with a biogenic precursor: monoterpenes ( $\alpha$ -pinene,  $\beta$ -pinene, limonene, and  $\Delta^3$ -carene) and one terpenoid alcohol (terpinene-4-ol). They found  $\alpha$ -pinene SOA was the least active CCN and limonene SOA exhibited the strongest CCN activity. The oxidation mechanisms are essential to determine the activation ability of their products and to investigate the role of monoterpenes in the cloud formation.

Because of the potential importance of some kinds of monoterpenes on the SOA formation, much of the research is related to elucidating the oxidation mechanisms. A lot of work has gone into investigating the gas-phase kinetics of  $\alpha$ - and  $\beta$ -pinene and sabinene reactions with OH and NO, ozone (see Kanakidou et al., 2004). Experimental conditions were varied to mimic several environmental conditions, such as  $\text{NO}_x$  photooxidation,  $\text{O}_3$  reaction or OH reaction. Seinfeld and Pankow (2003) have summarized laboratory studies on SOA formation, especially for oxidation pathways

of  $\alpha$ - and  $\beta$ -pinene and sabinene.

Oxygenated products capable of nucleation in the atmosphere should be characterized by low-volatility. The contributions of three major oxidation processes of  $\alpha$ - and  $\beta$ -pinene (OH, NO<sub>3</sub> and ozone) to new aerosol formation and aerosol yield have been found in laboratory studies to be different for these three possible reactions. Bonn and Moortgat (2002) found ozone has the highest potential to form new particles at similar reactant consumption rates of  $\alpha$ -pinene as well as for  $\beta$ -pinene. However, reactions of the monoterpenes with either OH or NO<sub>3</sub> result in remarkably less nucleation (Hoffmann, 2001). Kavouras et al. (1998) found some monoterpenes emitted by vegetation are photooxidized to DCA. DCA were the lowest volatile compounds positively identified in terpene's-generated aerosols. For both endo- and exocyclic monoterpenes, acylperoxy radicals are involved in the formation of DCA via permutation reactions with HO<sub>2</sub> or RO<sub>2</sub> radicals (Winterhalter et al., 2000; Koch et al., 2000; Jenkin et al., 2000). *Cis*-pinic acid (a C<sub>9</sub> dicarboxylic acid) has been identified as a condensed product of the ozonolysis of both  $\alpha$ - and  $\beta$ -pinene (Glasius et al., 2000; Kamens et al., 1999; Jaoui and Kamens, 2003a, b).

As one main component of BVOCs, limonene is around 5–20% of the total monoterpenes emission on mass basis (Griffin et al., 1999; Andersson-Skold and Simpson, 2001; Seinfeld and Pankow, 2003; Pio et al., 2005; Plaza et al., 2005). This reactivity makes *d*-limonene the important monoterpene from the perspective of aerosol formation potential. Andersson-Skold and Simpson (2001) estimated that 21.3% of SOA is formed from *d*-limonene, in contrast to  $\alpha$ - and  $\beta$ -pinene, however, our knowledge about gas-phase kinetics of the limonene reactions with ozone, OH and NO<sub>3</sub> radicals is far from complete.

There are only few papers on this topic (Grosjean

et al., 1992, 1993; Calogirou et al., 1999; Glasius et al., 2000; Larsen et al., 2001; Khamaganov and Hites, 2001; Li et al., 2002; Weschler and Shields, 2003; Fan et al., 2003; Liu et al., 2004; Leungsakul et al., 2004). Khamaganov and Hites (2001) measured and compared the rate constants for the gas-phase reactions of ozone with the biogenic hydrocarbons isoprene,  $\alpha$ - and  $\beta$ -pinene, and limonene over the temperature range 242–363 K and at 760 Torr total pressure (the Arrhenius expression for limonene is  $(2.95^{+0.77}_{-0.61}) \times 10^{-15} \exp[-\frac{783 \pm 72}{T}]$ ). Compared with the relative atmospheric residence times of these four biogenic hydrocarbons with the reactions of the different concentrations of ozone in remote region, rural region and urban place, Khamaganov and Hites (2001) found that limonene exhibited the smallest atmospheric residence time and was primarily removed by reactions with ozone, not OH. Li et al. (2002) investigated the organic aerosol formation in the office with strong indoor ozone source and *d*-limonene. They found a high concentration of hygroscopic secondary organic aerosols was generated in the presence of ozone (100 ppb) with *d*-limonene (240 ppb) at moderate humidity (RH = 28%). The particle number concentration reached a maximum of 26,000 particles cm<sup>-3</sup> in the 0.1–0.2  $\mu$ m size range about 30 min after initiating the experiment. Fan et al. (2003) examined the primary and secondary products resulting from reaction initiated by ozone (40 ppb) and *d*-limonene (1.7 mg m<sup>-3</sup>) in a controlled environment facility. They found the hydroxyl radicals (OH) generated from the O<sub>3</sub>/*d*-limonene reactions played an important role in chemical transformations.

However, the above studies mainly focused on the oxidation products. Until recently, most studies focused to understand oxidation mechanisms. Leungsakul et al. (2004) modelled the ozonolysis reaction of *d*-limonene. Both simulation and experimental results suggested that *d*-limonene ozonolysis generates a significant amount of OH, which cannot be explained by the hydroperoxide channel alone. A major product, limononaldehyde, was identified as well as keto-limonene, keto-limononaldehyde, limononic acid and keto-limononic acid. For the particle phase, keto-limononaldehyde was found to be the most abundant product in the particle phase. As experiments on the CCN ability of each aerosol product, or that of limononic acid (semi-volatile products) which can partition onto existing particles, do not exist, we still do not know which compound contributes to CCN.

### 3.2.2. Oxidation of soot

Soot, a form of the material commonly referred to as BC, originates from combustion processes and is a mixture of EC and OC. Bond et al. (2004) estimated global emissions of BC in the year 1996 were 1.6, 3.3 and 3.0 Tg C yr<sup>-1</sup> for biofuel, vegetation fires and fossil fuel burning, respectively.

The freshly emitted soot is extremely hydrophobic. However, through soot aging soot becomes less hydrophobic. Chughtai et al. (1991, 1996, 1999) observed that oxidation processes generates oxygen-containing functional groups, increasing the polarity of soot surfaces. Kotzick and Niessner (1999) observed that activation of soot particles to cloud droplets after reaction with ozone occurred at lower supersaturation and concluded that this was due to the presence of polar oxygen-containing functional groups on the surface of the particles. Lary et al. (1999) proposed that carboxylates could be produced in this process and cause soot particles to become more hydrophilic. Decesari et al. (2002) found that the soot oxidation process causes the formation of water-soluble polycarboxylic compound (HULIS).

Recently, Zuberi et al. (2005) demonstrated the CCN ability of the aged soot under two oxidation conditions. One of the oxidation processes exposed soot to OH/O<sub>3</sub>/H<sub>2</sub>O/UV, in which ozone is 20 ppm and the concentration of OH is  $4 \times 10^{10}$  molecule cm<sup>-3</sup>, by using a Hg UV lamp at 254 nm, at RH 60% and 1 atm for 30 min. The aged soot was observed to be activated at 272% supersaturation. The second process exposed soot to concentrated HNO<sub>3</sub> at approximately



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<https://www.sciencedirect.com/science/article/pii/S135223100500498X>

3.8 Torr  $\text{HNO}_3$  partial pressure at room temperature in a sealed vessel for 45 min. This time, the aged soot was activated at 172% supersaturation. Based on these results we can speculate that aged soot may not be neglected in the cloud formation processes, which subsequently change the scavenging mechanisms of soot. Recently, Molina et al. (2004) identified another removal pathway where- by the organic surface (alkane and aromatic), on atmospheric particles is degraded by oxidation initiated by hydroxyl radicals (OH), which leads to rapid volatilization. The efficiency of this process appears to be comparable to that of precipitation removing organic aerosols from atmosphere (Stephanou, 2005). Some preliminary results of methane-soot oxidation studies also indicate efficient carbon loss (Molina et al., 2004). Therefore a carbon loss mechanism may be applied to describe the atmospheric oxidation of soot and the influence on the aging process of soot. This interesting area should be studied further.

### 3.3. Improvement of CCN ability of atmospheric aerosols by oxidation of organic coatings

Recent field measurements have shown that a significant fraction of both continental and marine inorganic aerosols (sea salt, dust and sulfate) are coated by organic films (Tervahattu et al., 2002a, b; Russell et al., 2002; Tervahattu et al., 2005). This widespread occurrence of mixed organic and inorganic species within the same particle implies a broad impact of the organic chemical and physical properties on the atmospheric aerosols. Organic coatings can modify the particle hygroscopicity, CCN abilities and heterogeneous chemical reactivity (Saxena et al., 1995; Cruz and Pandis, 1998; Facchini et al., 1999a, b). Rudich (2003) reviewed the laboratory experiments on the physical and chemical processes of particles with high organic content and particles with surface-active organic coatings. Additional studies have since been published.

The main reported organic coatings are fatty acids of different carbon chain length up to the  $\text{C}_{32}$  in continental aerosols (mainly *n*-alkanoic acids with evidence for *n*-alkenoic acids) and inverted micelle structure with relatively short carbon chains in marine aerosols (Ellison et al., 1999; Tervahattu et al., 2002a, b, 2005). Fatty acids can be considered as potentially important aerosol surfactants because they are major components of many anthropogenic and natural atmospheric emissions (Tervahattu et al., 2005). Large amounts of fatty acids are released from biomass burning (Oros and Simoneit, 2001; Simoneit, 2002). Oros and Simoneit (2001) measured high emissions of longer-chained fatty acids from biomass burning. The longer-chained fatty acids are expected to have a hydrophobic property that will influence CCN ability of the mixed aerosols. However, they contain one or more carbon-carbon double bonds, which are susceptible to oxidative attack by all of the important atmospheric oxidants such as OH,  $\text{O}_3$ ,  $\text{NO}_3$  and halogens. The oxidation process on the surface of organic films will alter the properties of the aerosols, such as a propensity to uptake water and nucleate cloud formation (Demou et al., 2003).

Very recent experimental work has indicated that an increase in CCN ability of one kind of fatty acid (oleic acid) aerosols results from exposure to ozone (Broekhuizen et al., 2004a, b). Katrib et al. (2004) studied heterogeneous reactions of oleic acid aerosol particles with ozone, and found that this oxidation process increased the carbon-normalized oxygen content ( $z/x$ ) of the average chemical composition  $\text{C}_x\text{H}_y\text{O}_z$  of the particle. Recently, Hung et al. (2005) also studied the reaction of oleic acid with ozone and nitrate radicals. High molecular weight molecules are formed in their experiments, suggesting particle hygroscopicity and effectiveness as CCN increases during transport and chemical reactions of particles with atmospheric oxidants. They also suggested these high molecular weight products (HULIS) have low vapour pressure and may be surface active and thus lower the surface tension of partially activated droplets.

Meanwhile, there are some experimental studies on the heterogeneous reaction between the gas-phase ozone and oleic acid film. King et al. (2004) studied the reaction of ozone with individually optically levitated droplets of oleic acid and aqueous sea salt. Their results show the oxidation of organic films results in the droplets become more hydrophilic, with the major products being nonanoic acid and nonanal. Thornberry and Abbatt (2004) also investigated the gas-surface reaction between the ozone and liquid unsaturated fatty acids (oleic acid, linoleic acid and linolenic acid) and concluded that this kind of heterogeneous reaction is a facile one, proceeding considerably faster on a collision basis than that in the gas phase. Analysing the infrared spectra of the films measured after variable exposures to ozone, Asad et al. (2004) suggested the condensed products are more likely HULIS than azelaic acids which were identified as a liquid-phase reaction product following the reaction of ozone with oleic acid (Moise and Rudich, 2002).

The molecular dynamics simulations on the uptake of gas phase ozone and the collision rate between ozone and double bonds at unsaturated organic interfaces with vapour have also been studied (Vieceli et al., 2004). The self-assembled monolayer (SAM), which represents an organic layer adsorbed on an inorganic core, has characteristics similar to those of a solid surface. Although uptake into the organic phase does not occur in the SAM, the van der Waals interaction between ozone and SAM results in a significant residence time in the surface region. Shortly after this paper, the kinetics measurements supported the view that ozone has significant residence time on the surface (Dubowski et al., 2004). The contact angle of water droplet resting on a SAM will decrease after exposure to ozone because more polar species formed on the surface contributes to an increase in surface hydrophilicity (Dubowski et al., 2004).

In summary, as for main inorganic CCN, some sulfate aerosols and sea salts covered by hydrophobic surfactant organic films were observed in nature, which can lead to impacts on the chemical and physical properties of aerosol

particles. The oxidation processes are expected to occur on organic aerosols during their residence in the atmosphere. However, the potential to become active CCN under atmospheric conditions may also depend on their residence time in the atmosphere, the concentration of atmospheric oxidants, and the rate of such heterogeneous oxidation reactions. There also remains an open question of the global importance of organic films on inorganic CCN, which depends on how commonly particles are covered by such surfactants and how extensive the coverage of the organic films is.

#### 4. Experimental studies on activation capability of pure OC

Sulfates (e.g.,  $(\text{NH}_4)_2\text{SO}_4$ ) are thought to be the dominant component of CCN (Pruppacher and Klett, 1997) and the mass concentration of DCA in the atmosphere has been estimated to be  $\leq 1/10$  of the mass of non-seasalt sulfates (Hori et al., 1990; Husain and Dutkiewicz, 1990; Joos and Baltensperger, 1991; Kawamura and Usukura, 1993; Khwaja, 1995; Limbeck and Puxbaum, 2000; Loflund et al., 2002; Savoie et al., 1994; Sempere and Kawamura, 1994; Voisin et al., 2000). However, real particles in the atmosphere can be a mixture of various inorganic and OC, and hence exhibit very complex physical properties (e.g., solubility, surface activity, hydrophobicity and morphology). Thus, despite the relatively low mass concentration of DCA, their roles as CCN have been taken very seriously. In recent years, studies have provided experimental data on the activation capability of single-component organic aerosols (Table 2), considered to be the first step in evaluating the role of DCA in cloud formation.

##### 4.1. Hygroscopic growth theory for OC

The equilibrium droplet size and cloud nucleating properties of an aerosol particle under cloud conditions are most commonly described by the Kohler equation. Chylek and Wong (1998) interpreted the equation as

$$S = \frac{P}{P_\infty} - 1 = a(M) \exp\left(\frac{2\sigma_{\text{solution}}M_w}{r\rho_{\text{solution}}RT}\right) - 1 \quad (1)$$

and

$$a(M) = \frac{m_w}{m_w + im_s\left(\frac{M_w}{M_s}\right)} \quad (2)$$

where  $P$  is the equilibrium water vapour pressure of the droplet,  $P_\infty$  is the equilibrium vapour pressure over a flat water surface,  $a(M)$  is the water activity in solution,  $\sigma_{\text{solution}}$  is the surface tension of the solution,  $\rho_{\text{solution}}$  is the density of the solution,  $M_w$  is the molecular weight of water,  $M_s$  is the molecular weight of the solute,  $i$  is van't Hoff factor, and  $R$  and  $T$  are the ideal gas constant and temperature, respectively. Several variations to Kohler's equation have been proposed (Doyle, 1961; Fitzgerald and Hoppel, 1984; Hanel, 1976; Konopka, 1996; Mason, 1971; Pruppacher and Klett, 1997; Reiss, 1950). The new developments aim to account for the complex chemical composition of aerosol particles, the dissolution of gases into droplets and the physical and chemical properties of the droplet solutions. Laaksonen et al. (1998) have incorporated the effects of soluble trace gases into the Kohler equation and further modified Eq. (1) to consider slightly soluble substances. Li et al. (1998) investigated the effect of soluble surfactant on aerosols containing inorganic solute, which requires detailed knowledge of the surfactant properties of the solute, including the critical micelle concentration and excess concentration on surfaces. However, this study was confined to sodium dodecyl sulfate and NaCl solute. The influence of charge on droplet growth and activation was considered by Wexler and Ge (1998), assuming a given surface at a fixed charge. They have concluded that, in a laboratory setting, surface charges on pure hydrophobic particles could cause growth and activation.

Insoluble matter can also affect CCN activation. Fletcher (1962) has developed a theory for water nucleation on insoluble spherical particles with uniform surfaces. Another more recent theory of cloud droplet formation on aerosol particles containing both soluble substances and a partially hygroscopic insoluble core has been developed by Gorbunov and Hamilton (1997). They found that the contact angle of the water solution on the surface of the insoluble core affected considerably the CCN activation. Soon after, CCN containing inorganic salts and various insoluble non-volatile organic substances, as well as surface-active agents, were reconsidered by Gorbunov et al. (1998), although no experimental results are available to evaluate the effectiveness of this model.

The classical Kohler theory is valid for aerosol particles consisting of water-soluble inorganic salts, which assumes a perfect water-absorbing surface. However, for soluble and slightly soluble organic substances classical Kohler theory neglects surface activity; namely, particle water uptake and surface tension reduction during the early droplet growth. Shulman et al. (1996) were first to present a modified version of the Kohler equation which contained solubility and surface tension for slightly soluble compounds. They concluded that any slightly soluble surface-active compound could affect cloud droplet growth by two processes: (i) causing gradual dissolution in the growing droplet, and (ii) lowering the surface tension of the droplet. In the following sections we discuss the effects of solubility, surface tension and van't Hoff factor on the activation of OC.

#### 4.1.1. Solubility

In order to discuss the influence of solubility on the organic activation, we can use the following equations with the assumption that only the dissolved organic solute has the 'Raoult's effect' (Raymond and Pandis, 2002):

$$\varepsilon = \frac{C_{sat}(D_p^3 - d_s^3)\rho_w}{d_s^3\rho_s} \quad (3)$$

and

$$a(M) = \frac{m_w}{m_w + i\varepsilon m_s \left(\frac{M_w}{M_s}\right)} \quad (4)$$

where  $\varepsilon$  is the water-soluble fraction of the dry particle,  $C_{sat}$  is the solubility of the slightly soluble compound (mass per volume). Eq. (5) can thus be used to describe the effect of small amounts of highly soluble ammonium sulfate on the critical supersaturation (to see the same method as Bilde and Svenningsson (2004)

$$a(M) = \frac{m_w}{m_w + i_o\varepsilon m_s\beta \left(\frac{M_w}{M_s}\right) + i_a(1 - \beta)m_s \left(\frac{M_w}{M_a}\right)} \quad (5)$$

where  $\beta$  is the mass fraction of slightly soluble organic material in the initial dry particle,  $i_o$  is the organic material van't Hoff factor,  $i_a$  is the van't Hoff factor of ammonium sulfate,  $M_a$  is molecular weight of ammonium sulfate.

We have plotted classical Kohler theory and several variations of this theory in Fig. 2 for existing literature data using a simple model (see Appendix A for further information). This figure illustrates that if we considered the solubility (Eq. (4)) in the Kohler equation (1) with constant van't Hoff factor ( $i = 1$ ), two maxima for supersaturation as a function of droplet diameter for adipic acid solution at  $T = 298.15\text{K}$  are predicted. This curve is very different from one that assumes adipic acid is completely dissolved (Eqs. (1) and (2)). There is a cusp at minimum droplet diameter, where all adipic acid is dissolved. However, if we consider the purity of adipic acid with mixture of 2% ammonium sulfate (Eq. (5)), the first peak decreases sharply. Bilde and Svenningsson (2004) experimentally confirmed these two maxima, and showed that a small amount of salt had a dramatic effect on critical supersaturation of slightly soluble OC.

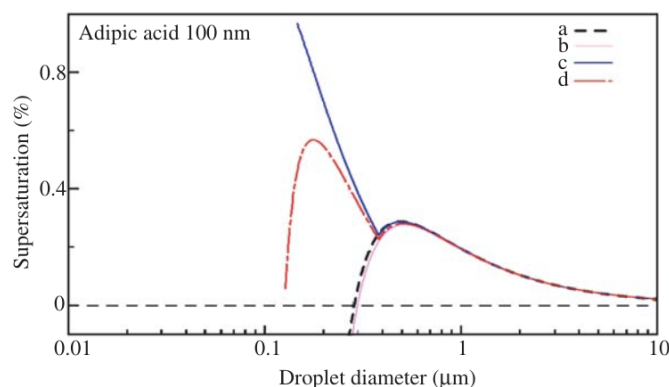


Fig. 2. Variation of supersaturation as a function of droplet size for adipic acid at 298.15 K. The following curves consider: (a) classical Kohler equation (1) (van't Hoff factor  $i = 1$ ), (b) Kohler equation (1) considering surface tension change with Eqs. (7) and (8) (Egeman et al., 2000; Alvarez et al., 1997), (c) Kohler equation (1) including limited solubility with Eqs. (3) and (4) (Raymond and Pandis, 2002), (d) Kohler equation (1) including limited solubility with Eq. (3) and modified Eq. (5) with 2% mass fraction of ammonium sulfate).

#### 4.1.2. Surface tension

An efficient theoretical method to determine the surface tension reduction of the droplet by various soluble OC with respect to water has yet to be developed. Some researchers have measured the surface tension at concentration levels typical of each species in the droplet at its activation diameter (Shulman et al., 1996; Raymond and Pandis, 2002). Meanwhile, in order to recreate the surface tension behaviour due to variation in the concentration of water-soluble organic compounds (WSOC) in a growing droplet, Facchini et al. (1999b) measured the surface tension of atmospheric droplet samples and found the cloud droplet surface tension varies as a function of dissolved organic carbon concentration and temperature:

$$\sigma = 72.8 - 0.018T \ln(1 + 628.14C) \quad (6)$$

where  $T$  is the temperature (in K) and  $C$  is concentration of soluble carbon in  $\text{mol L}^{-1}$ . Mircea et al. (2002) have modified Kohler equation based on this finding and found that CCN concentration can increase due to the decrease of the surface tension of droplets. However, this relationship does not take into account the differences various OC have on surface tension reduction. The surface tension reduction with respect to water not only depends on the concentration of OC, but also the nature of organic molecules (Shulman et al., 1996; Raymond and Pandis, 2002).

Egeman et al. (2000) tested 44 OC to determine the role of simple and valence molecular connectivity, octanol-water partition coefficient and atom/bond contributions in surface tension. They found that chemical content was highly significant in the surface tension calculation and proposed the following method to estimate the surface tension for the OC:

$$\sigma = 14.92 + \sum_{i=1}^{i=m} n_i \times A_i, \quad (7)$$

where  $m$  represents the number of various types of atoms/bonds and  $n$  represents the count of each type of atom/bond in the molecule, and  $A_i$  defined atom/bond contributions. As for soluble, surface-active OC, their impact on the surface tension of a water droplet depends on their own surface tension properties. Alvarez et al. (1997) measured surface tension of binary mixtures of organic acids with water in different mass fraction of solute at the range of temperature between 20 and 50°C, and the following fitting Eq. (8) was obtained:

$$\frac{\sigma_2 - \sigma}{\sigma_2 - \sigma_1} = \left(1 + \frac{ax_2}{1 - bx_2}\right)x_1, \quad (8)$$

where  $\sigma_2$  and  $\sigma_1$  the surface tensions of pure water and pure acid respectively,  $x_1$  and  $x_2$  are the mole fractions of acid and

water, and  $a$  and  $b$  are the fitted parameters which are linear functions of temperature for each acid. In order to evaluate the impact on surface tension by organics, we modified Eq. (1) with (7) and (8) and obtained the new Kohler curve for adipic acid at  $T = 298.15$  K in Fig. 2, which indicates critical supersaturation decreases slightly compared to the case of constant surface tension where pure water is assumed. Interestingly, we also used Eq. (8) with the modified Kohler equation by Young and Warren (1992) and the results shows the critical supersaturation increases significantly comparing with constant surface tension of water due to correction term  $\partial s = \partial m$  which contributes the increment of critical supersaturation, as the surface tension increases with the increase of droplet mass. However, Chylek and Wong (1998) pointed to a potential misunderstanding by Young and Warren (1992) as this correction term can be cancelled out by two other terms.

#### 4.1.3. Van't Hoff factor

The van't Hoff factor,  $i$ , accounts for the dissociation of the solute and the non-ideal behaviour of the solution. It represents the number of dissociated species per solute molecule that would form if the solute were dissolved in an infinitely dilute solution. The van't Hoff factor is often an empirically determined correction factor, for example, Low (1969) calculated the values of  $i$  for many inorganic compounds. In several studies, the van't Hoff factor for inorganic salts are simplified and approximated as the constant values (Young and Warren, 1992). However, Chylek and Wong (1998) found that the Kohler equation with constant van't Hoff factor led to considerable errors at high relative humidities, whereas with variable van't Hoff factors, the Kohler equation provided a better agreement with experimental data. However, very little information exists about the van't Hoff factors for OC. Since most OC do not dissociate significantly (solubility  $< 0.1$  M), the values for  $i$  is always assumed to be equal to unity (Corrigan and Novakov, 1999; Cruz and Pandis, 1997; Hori et al., 1990; Kumar et al., 2003; Prenni et al., 2001; Raymond and Pandis, 2002; Giebl et al., 2002).

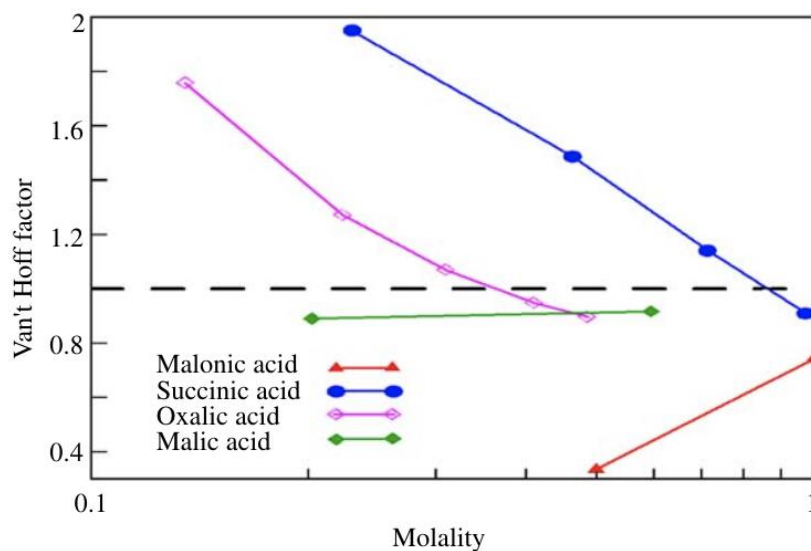


Fig. 3. Variation of van't Hoff factor with the change of molality for four organic compounds (using Eq. (2),  $a_w$  measured by Maffia and Meirelles (2001)).

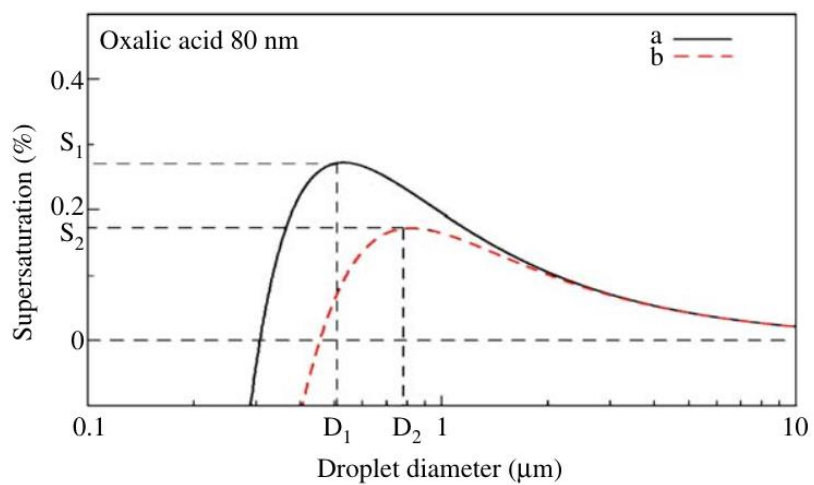


Fig. 4. Kohler curves at constant van't Hoff factor and variable van't Hoff factors, with the change of oxalic molality at 298.15 K. ((a) using constant van't Hoff factor,  $i = 1$ , (b) using the variable van't Hoff factor).

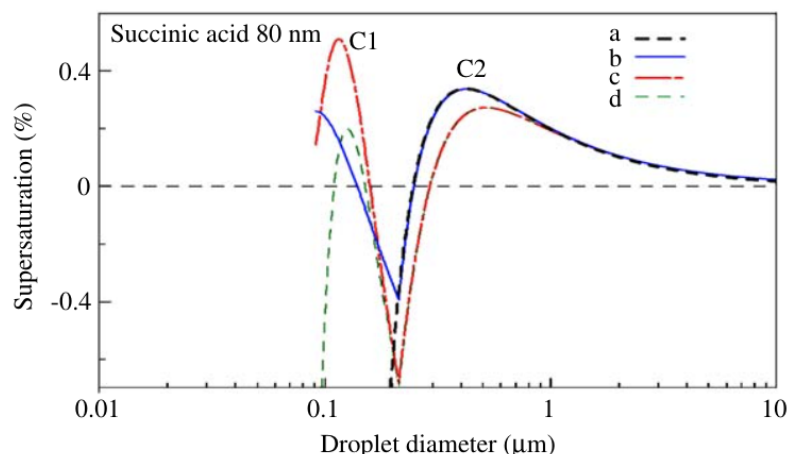


Fig. 5. Modified Kohler curves modified to take account of the limited solubility, mixture and van't Hoff factor change for succinic acid molality at 298.15 K. (a) Kohler equation (1) with constant van't Hoff factor  $i = 1$ , (b) Kohler equation (1) to take account of limited solubility (Raymond and Pandis, 2002) with constant van't Hoff factor  $i = 1$ , (c) Kohler equation (1) to take account of limited solubility (Raymond and Pandis, 2002) and van't Hoff factor change with succinic acid molality (Chylek and Wong, 1998), (d) taking account of limited solubility (Raymond and Pandis, 2002) and modified equation with mixed 2% mass fraction of ammonium sulfate as the method as Bilde and Svenningsson (2004) and considering variable van't Hoff factor with the change of succinic acid molality as the method as Chylek and Wong (1998).

In recent years some researchers measured and calculated the water activity using modified UNiversal quasicheMical Functional group Activity Coefficient (UNIFAC) model in aqueous polycarboxylic acid systems (Maffia and Meirelles, 2001; Peng et al., 2001). To evaluate the importance of van't Hoff factor, we employed Eq. (2) (Low, 1969; Young and Warren, 1992) for oxalic, succinic, malonic and malic acid at molality range of 0.1–1.0 M. The results are plotted in Fig. 3.

The critical supersaturation is clearly different using the constant van't Hoff factor as opposed to the variable van't Hoff factor (Fig. 4). Taking into account the solubility and van't Hoff factor change with molality, we simulated the process of activation for the slightly soluble dry succinic acid (Figs. 5 and 6). The Kohler curves still have bimodal behaviour and the first peak decreased largely with the mixture of 2% mass fraction of ammonium sulfate.

#### 4.2. Organic-compound ability to act as CCN

Although much work has been done to improve theories describing CCN activation for OC (Shulman et al., 1996; Gorbunov et al., 1998), to our knowledge predictions of the classical Kohler theory are the most widely used for comparison with actual experimental findings (Table 3). In this section, we compare different experimental works and examine them against the classical theoretical predictions and modified theory considering the solubility, variable van't Hoff factors and impurity in the activation process of several atmospherically important DCA.

#### 4.2.1. Oxalic acid ( $HO-C(O)-C(O)-OH$ )

Oxalic acid is moderately soluble in water and has a high vapour pressure (Table 2). A good agreement exists between most experiments in the studies by Kumar et al. (2003) and Giebl et al. (2002) and the modified

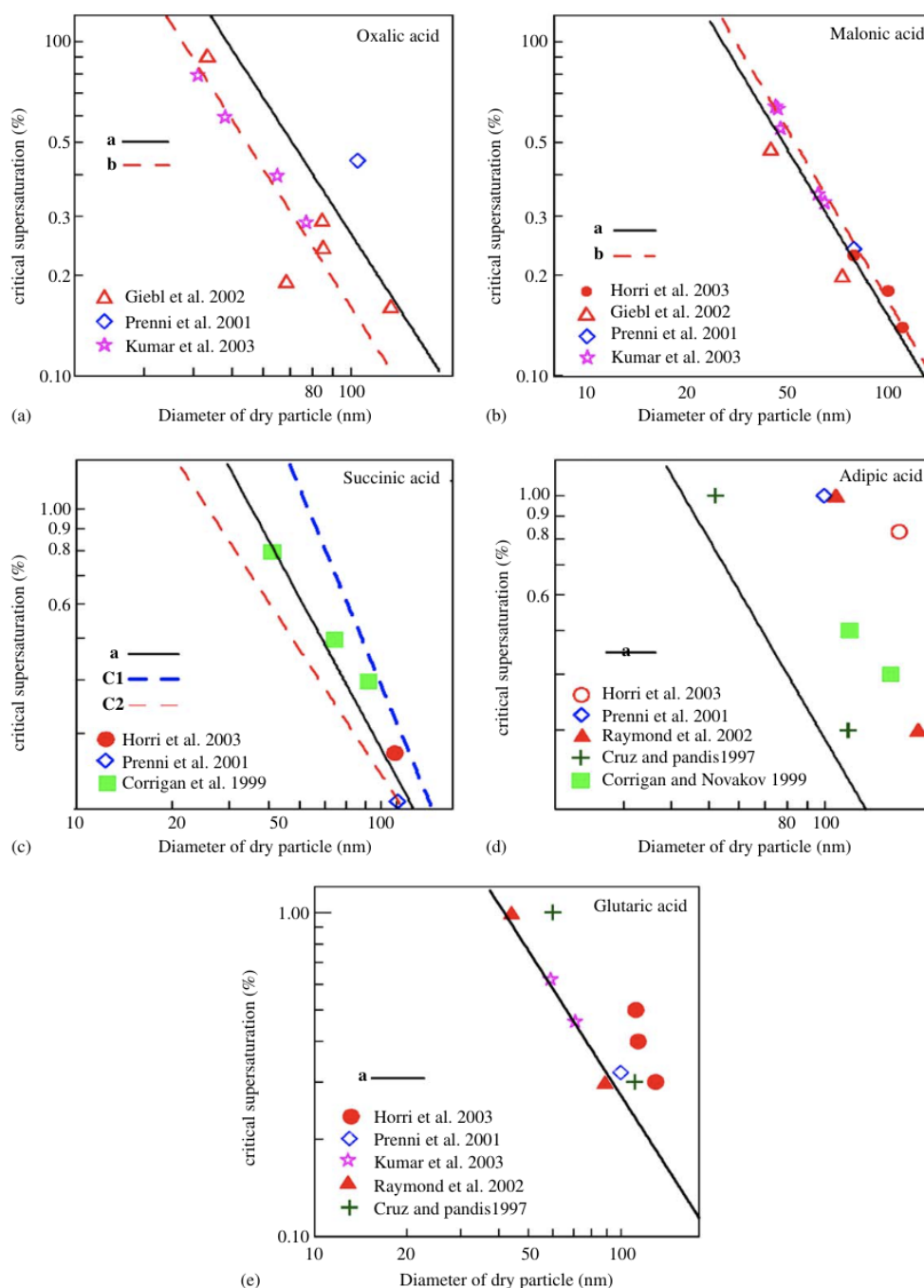


Fig. 6. (a–e) The relationships between the activation supersaturations of dicarboxylic acids and their dry particle diameters obtained from experimental results and theoretical predications, (a) the Kohler equation (1) with constant van't Hoff factor,  $i = 1$  (black line); (b) the Kohler equation (1) with the variable van't Hoff factor (red line); (c1) the first maximum using Kohler equation (1) with the variable van't Hoff factor (dotted blue line); (c2) the second maximum using Kohler equation (1) with the variable van't Hoff factor (dotted red line). For interpretation of the references to colour please refer to the online version.



Table 3  
 Literature data on the activation experiment for organic compounds

| Study                       | Methodology <sup>a</sup> | Growth Theory   | Tested organic acids   | Active organic acids <sup>b</sup>                       |
|-----------------------------|--------------------------|---|--|---|
| Cruz and Pandis             | DMA & CCNC               | Kohler (1936)   | Glutaric, adipic   | Glutaric, adipic  |
| Corrigan and Novakov (1999) | DMA & CCNC               | Fitzgerald and Hoppel (1984)                                      | Succinic, adipic, glucose  | Succinic, adipic, glucose                               |
| Prezzi et al. (2001)        | DMA & CCNC               | Ming and Russell (2001)   | Oxalic, malonic, succinic, adipic, glutaric  | Oxalic, malonic, succinic, adipic, glutaric             |
| Ramond and Pandis (2002)    | DMA & CCNC               | Hanel (1976); Laaksonen et al. (1998); Seinfeld and Pandis (1998) | Adipic, cholesterol, glutaric, hexadecane, stearic, hexadecanol, leucine, myristic, pinonic, palmitic, norpinic, glutamic, pinic | Glutaric, adipic, pinic, cholesterol, norpinic, pinonic |
| Hori et al. (2003)          | TGDCC & CEM              | Mason (1971)  | Malonic, succinic, adipic, glutaric, malic, phthalic   | Malonic, succinic, adipic, glutaric, malic, phthalic    |
| Kumar et al. (2003)         | TGDCC & DMA              | Pruppacher and Klett (1980)                                       | Oxalic, malonic, oleic, glutaric, stearic  | Oxalic, malonic, glutaric                               |

<sup>a</sup>DMA: differential mobility analyzer; CCNC: cloud condensation nuclei counter; TGDCC: thermal gradient diffusion cloud chamber; SEM: scanning electron microscope.

<sup>b</sup>Active organic acids are defined as organic compounds in which active dry diameters are no more than 0.15  $\mu\text{m}$  under the condition of supersaturation no more than 1%.

theoretical activation diameters considered the van't Hoff factor change with molality for oxalic acid (Fig. 6a). Prezzi et al. (2001) observed, however, a significant disagreement between the theoretical and experimental values. Factors such as experimental conditions (residence time and relative humidity) and conversion into oxalic dihydrate could not entirely explain this disagreement. Hori et al. (2003) suggested this difference might be related to the evaporation losses of solid particles in the experimental systems of Prezzi et al. (2001). Seemingly, the hygroscopic behaviour of oxalic acid can be predicted by the modified Kohler equation. Furthermore, oxalic acid exhibits the highest CCN ability among the other DCA, comparable to that of ammonium (Hori et al., 2003).

#### 4.2.2. Malonic acid ( $\text{HO}-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-\text{OH}$ )

Malonic acid has high water solubility and vapour pressure (Table 2) and thus is expected to have high CCN activity. Since the evaporation losses occur under low humidity conditions, the activation capability of malonic acid should be determined, optimally, under relatively high humidity. Hence, the vaporization losses are expected to be substantially suppressed. When the solute evaporation is suppressed due to moderately humid conditions, malonic acid can thus be considered to act as an effective CCN. Experimental values (Kumar et al., 2003; Prezzi et al., 2001; Hori et al., 2003; Giebl et al., 2002) were more consistent with the modified theoretical predictions that considered the van't Hoff factor change as show in Fig. 6b. Note that since the van't Hoff factor is below 1 around the critical activation diameter, the modified predictions are greater than classical predictions.

#### 4.2.3. Succinic acid ( $\text{HO}-\text{C}(\text{O})-(\text{CH}_2)_2\text{C}(\text{O})-\text{OH}$ )

Succinic acid has moderate solubility in water and moderate vapour pressure (Table 2). Succinic acid deliquescence is close to 100% relative humidity (Parsons et al., 2004). Under low humidity conditions the dry particles of succinic acid seems to follow the initiation peak of the deliquescence, i.e., deviated from the Kohler curve (Hori et al., 2003). On the contrary, under humid conditions the observations scatter between the first peak  $C_1$  and second peak  $C_2$  of modified Kohler equation with variable van't Hoff factor (Fig. 6c), which can be explained by the purity of succinic acid. If the succinic acid is fully pure, the critical supersaturation will be at  $C_1$  (Fig. 5).

#### 4.2.4. Adipic acid ( $\text{HO}-\text{C}(\text{O})-(\text{CH}_2)_4\text{C}(\text{O})-\text{OH}$ )

The CCN activity of adipic acid has also been frequently investigated (Table 3). Due to its relatively poor water-solubility

(Table 2) and surface hydrophobicity, it is reasonable to say that adipic acid has a low CCN ability (Raymond and Pandis, 2002). The experimental critical supersaturations are significantly dispersed above the line of the classical Kohler curve. Since there is an activation barrier for the undissolved core of pure adipic acid (Fig. 2), the activation of adipic acid is most likely contributed to the impurity of adipic acid or supersaturated solution of the particle, which is confirmed experimentally by Bilde and Svenningsson (2004). While some small, varying amounts of salts may mix with adipic acid, the experimental results show no regular changes. Without water activity data for adipic acid, the Kohler equation with constant van't Hoff value are expected to yield erroneous results.

#### 4.2.5. Glutaric acid ( $\text{HO}-\text{C}(\text{O})-(\text{CH}_2)_3\text{C}(\text{O})-\text{OH}$ )

Glutaric acid has a high water-solubility comparable to that of ammonium sulfate. It also has a high vapour pressure (Table 2). Even under humid experimental conditions significant vaporization losses of particles can occur. Thus, somewhat erratic and unexpected activation behaviour has been observed in the course of experiments (Hori et al., 2003; Raymond and Pandis, 2002). For instance, Hori et al. (2003) have suggested that glutaric acid has a relatively low CCN capability due to its high activation supersaturations; while Kumar et al. (2003) have proposed that glutaric acid could activate at slightly smaller diameters. The comparison of literature results shows that experimental activation diameters are always larger than those predicted by the Kohler equation (1) with constant van't Hoff factor. Prenni et al. (2001) attributed this inconsistency to evaporation losses of particles. However, the variation of van't Hoff factor may be for another contributing factor.

#### 4.2.6. Malic acid ( $\text{OHC}(\text{O})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH}$ )

Malic acid has high solubility in water (Table 2). Hori et al. (2003) have shown that the theoretical activation of malic acid was quite consistent with experimental values and exhibited a high CCN ability. Since the van't Hoff factor is close to unity, the classical Kohler equation provides a good agreement with experiment data, as demonstrated in Fig. 2.

#### 4.2.7. Phthalic acid ( $\text{C}(\text{O})\text{OH}-\text{C}_6\text{H}_4-\text{C}(\text{O})\text{OH}$ )

Phthalic acid has very low solubility in water (Table 2) (Saxena and Hildemann, 1996). However, the experimental values indicate that it exhibits high CCN ability (similar to malic acid) (Hori et al., 2003). Although, the role of impurities can contribute to this high CCN ability, experimental studies of phthalic acid are desired. As for stearic acid ( $\text{C}_{18}\text{H}_{36}\text{O}_2$ ) and oleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ), they are both insoluble and cannot activate at supersaturations of 0.6% with dry diameters up to 140 nm (Raymond and Pandis, 2002).

#### 4.2.8. Factors influencing the activation of OC

In the atmosphere, supersaturation occurs naturally below 1% during normal cloud processes. For typical cumulus conditions, water supersaturations may reach values of over 10% through interactions between cloud droplets and the small-scale structure of atmospheric turbulence (Shaw, 2000). Note that most researchers have performed their experiments at different supersaturations. In order to compare the activation capability for different OC, we herein describe active organic acids as those for which active dry diameters are no more than 0.15  $\mu\text{m}$  under 1% supersaturation or less. Thus, we find that with a critical supersaturation lower than 1%, soluble organic acids can be expected to activate preferentially into cloud droplets (Table 3). The solubility is one of the most important driving factors determining CCN ability of a given organic compound. The decrease of critical supersaturation through surface tension change by organics is another important factor we demonstrated in our predicted results based on available literature. We also found that some other organics, having a finite contact angle with water, may serve actively as CCN, such as cholesterol (Table 2). Raymond and Pandis (2002) have suggested that the ability of a pure organic species to activate may depend not only on its solubility in water, but also on its ability to spread or form a finite contact angle with water. Moreover, in contrast to the studies on adipic acid, the experimentally derived critical supersaturations for slightly water-soluble compounds could depend significantly on the initial condensation stages of the particle phase (solid or liquid) (Hori et al., 2003). Our predicted results suggested that the control of the initial particle phase in the experimental system is of critical importance for experiments on the hygroscopic behaviour of less soluble particles. The initial particle phase could thus be considered a key factor in the evaluation of the actual CCN ability for such less soluble compounds in the real atmosphere. In addition, Hori et al. (2003) suggested that the morphology of the solid particles could be another important factor, since the crystallization and highly non-spherical shape of particles may enhance solubility. As for the particles which are volatile and distributed partially in the gas phase, such as oxalic acid, the condensation effect of volatile compounds should be included (Hori et al., 2003), since re-condensation of organic acid vapours on

existing droplets could promote droplet growth. This is similar to the condensation effect of nitric acid (Laaksonen et al., 1998). Broekhuizen et al. (2004a, b) studied the activation of pure oleic acid particles at different ozone concentrations, their results indicated that these particles became more active CCN species in the presence of ozone. In summary, solubility, organic volatility, morphology, surface tension, as well as the hydrophilic or hydrophobic nature of particles, and the oxidation process could be key factors in the theoretical prediction of the CCN ability of OC and the interpretation of experimental results.

The hygroscopic growth for many other atmospherically important organic acids is not known. Recent studies on the composition of single aerosol particles have indicated a high degree of internal mixing, i.e. inorganics and soluble primary organics or secondary are commonly detected in the same particle and it is likely that both species simultaneously contribute to the cloud nucleating ability of the tropospheric aerosol (Murphy et al., 1998). Indeed, ambient atmospheric aerosols contain small amounts of many different organic and inorganic species. Pruppacher and Klett (1997) and Saxena et al. (1995) suggested that CCN could be a mixture of inorganic and organic species. Our predicted results show slightly soluble organics mixed with inorganics can decrease the critical supersaturation (Fig. 3). Interestingly, through an adiabatic parcel modelling study for cloud droplet nucleation based on laboratory findings, Lohmann et al. (2004) indicated that small amounts of a soluble aerosol, such as ammonium sulfate, significantly decreases the activation diameter of moderately soluble organic aerosols. Furthermore, the high supersaturation in convective cumulus weather systems may also result in much more slightly soluble organic aerosols activated.

#### 5. (Bio) Chemical reactions altering CCN ability of organics

Bacteria are important, not only for their capability as CCN and IN, but for their potential role in the modification of other atmospheric OC that act as CCN. Bacterial utilization of formic and acetic acid in rain water was shown by Herlihy et al. (1987). DCA can also be efficiently transformed by bacteria and fungi in the boundary layer, with estimated degradation lifetimes comparable to major atmospheric oxidants (Ariya et al., 2002; Ariya and Amyot, 2004; Cote and Ariya, 2004a, b). Chemical transformation in the presence of airborne fungi has been observed with regard to seven different DCA (Ariya et al., 2002). Apparent reaction rates have been found to be a function of organic acid used (Ariya et al., 2002) and type of airborne fungi (Cote and Ariya, 2004a, b). Solution pH and temperature can be among the major factors contributing to the apparent reaction rate for microbiological degradation. Product analysis of the reaction mixtures indicate that several products that were non- or slightly toxic compounds, such as acetamide, acetoacetic, butanoic, and propionic acids, were formed after microbiological exposure (Ariya et al., 2002). Volatile species such as aromatics or heterocyclics, including carbonyl, hydroxyl and CN-substituted compounds, were also observed in infected samples using liquid and gas chromatography with mass spectrometric detection. Some of these identified chemicals (e.g., kojic acid and aflatoxin B1) are highly toxic and carcinogenic. Cote and Ariya (2004a, b) discovered that different fungi species drive microbiological degradation of several atmospherically active OC at very different rates. This degradation is also a function of several environmental factors, namely pH, temperature and nutrient levels. They also found that the presence of airborne taxa in organic solution alters the composition of the OC. This can be due to possible desorption processes, hinting that the collision of OC with bioaerosols modifies the chemical composition, and consequently the CCN ability of non-biological OC. Therefore, the role of bacteria and fungi in the chemical transformation of OC in atmosphere should not be neglected.

Clouds and fog provide a good culture medium for bacteria and fungi as increases in their concentrations have been observed (Fuzzi et al., 1997; Bauer et al., 2002). This can be ascribed to the abundant MCA and DCA in clouds and fog and the shelter they provide from damaging UV radiation (Sommaruga et al., 1997). Cloud water at the Sonnblick Observatory contained rather high amounts of organic acids, i.e. up to 0.3 mg l<sup>-1</sup> of formate and 2.1 mg l<sup>-1</sup> of acetate (Brantner et al., 1994). Collett et al. (1999) used Californian fog samples to show that the sum of formaldehyde, formate, acetate, propionate, pyruvate and oxalate concentrations comprised from 9% to 32% of the total organic carbon (TOC) content. Herckes et al. (2002) showed the sum of formate and acetate concentrations in fog water was more than 10% of the total organic carbon. Meanwhile, Fuzzi et al. (1997) showed that the concentration of cultivable bacteria and fungi reached values up to two orders of magnitude higher in fog than in clear air. However, the concentrations of cultivable bacteria in fog and clouds are different. Po Valley fog (Italy) had about 75 times more bacterial colonies and fungi (Fuzzi et al., 1997) than clouds at Mt. Rax (Bauer et al., 2002), meaning fog provides a more favourable culture condition for bacteria, resulting in a higher increased bacterial concentration in fog than in clouds. The role of bacteria may thus be more important in fog, since more available bacteria can act as fog condensation nuclei. This assumption is reasonable given that more than half of fog nuclei are water insoluble (Kuroiwa, 1951).

#### 6. Concluding remarks

The available literature data indicates that selected OC (e.g., MCA, DCA and HULIS) are predominant OC forming CCN. These molecules have several sources, including the marine pathways that deserve further consideration in future. Classical Kohler theory appears to have limited success in describing the hygroscopic behaviours of pure DCA. van't Hoff factor variation with the concentration of solute and solubility, in case of slightly soluble organics should be considered. Other factors such as surface tension, volatility, morphology, contact angle, deliquescence, and the oxidation process should be considered as potential key players in the theoretical prediction of the CCN ability of OC, and the interpretation of experimental results. Bacteria can act as CCN and derive chemical transformation of non-biogenic organic CCN. However, there are still numerous open questions regarding organic and bioaerosols (not only bacteria and fungi, but also pollen, cellulose and metabolites), (a) their significance as effective CCN in the real atmosphere and their ability to produce/reduce the number of metabolites that act as such, (b) water activity of many atmospheric organics and the mixture of inorganic and organic should be investigated, (c) hygroscopic growth mechanisms particularly for complex and chemically heterogeneous mixtures, (d) the nature of reactions at surfaces as well as interfaces, atmospheric chemistry induced by bioaerosols, (e) proper identification and quantification of chemical composition of aerosols (i.e., development of novel selective and high sensitive measurement techniques), and (f) detailed mechanisms for chemical/biochemical transformation processes under various environmental conditions should be performed to adequately evaluate the importance of organic aerosols, including bioaerosols, in the chemistry and physics of the atmosphere.

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#### Appendix A. Model code description

We employed a simple model to integrate the existing experimental and theoretical literature on CCN ability of OC. A few main features are described below.

##### A.1. Solubility

Solubility is calculated using the following formulas:

$$S = \frac{P}{P_{\infty}} - 1 = a(M) \exp\left(\frac{2\sigma_{\text{solution}}M_w}{r\rho_{\text{solution}}RT}\right) - 1$$

$$\varepsilon = \frac{C_{\text{sat}}(D_p^3 - d_s^3)\rho_w}{d_s^3\rho_s}$$

$$a(M) = \frac{m_w}{m_w + i\varepsilon m_s \left(\frac{M_w}{M_s}\right)}$$

$T = 298.15 \text{ K}$ ,  $s = 72.8 \text{ mN m}^{-1}$ ,  $R = 461.5 \text{ J kg}^{-1} \text{ K}^{-1}$ ,  $M_w = 18.01 \text{ g mol}^{-1}$ ,  $i = 1$ .

Molecular weight used in this model were for adipic acid: 146.14; succinic acid: 118.09; malonic acid: 104.06; malic acid: 139.03; oxalic acid: 90.00; and glutaric acid: 132.11 MW in  $\text{g mol}^{-1}$ . We used the solubility ( $C_{\text{sat}}$  ( $100 \text{ g soln}^{-1}$ ) of 0.025 and 0.083 from adipic and succinic acid, respectively, based on studies of Broekhuizen et al. (2004a, b); while the density for adipic and succinic acid was considered to be 1.36 and 1.552 ( $\text{g cm}^{-3}$ ). The radius of droplet by  $\Delta r = 0.001 \mu\text{m}$  was increased in every step.

##### A.2. Impurity effect

$$S = \frac{P}{P_{\infty}} - 1 = a(M) \exp\left(\frac{2\sigma_{\text{solution}}M_w}{r\rho_{\text{solution}}RT}\right) - 1$$

$$\varepsilon = \frac{C_{sat}(D_p^3 - d_s^3)\rho_w}{d_s^3\rho_s m_w}$$

$$a(M) = \frac{m_w + i_o \varepsilon m_s \beta \left(\frac{M_w}{M_s}\right) + i_a(1 - \beta)m_s \left(\frac{M_w}{M_a}\right)}{m_w}$$

$1 - \beta = 2\%$  (ammonium sulfate mass fraction),  $i_a = 3$ . The van't Hoff factor of ammonium sulfate;  $i_o = 1$  the organic material van't Hoff factor.

### A.3. Surface tension

We have employed the following formula for surface tension calculations:

$$S = \frac{P}{P_\infty} - 1 = a(M) \exp\left(\frac{2\sigma_{solution}M_w}{r\rho_{solution}RT}\right) - 1$$

$$a(M) = \frac{m_w}{m_w + im_s \left(\frac{M_w}{M_s}\right)}$$

Organic surface tension:

$$\sigma = 14.92 + \sum_{i=1}^{i=m} n_i \times A_i$$

Organic acids surface tension for adipic acid is considered to be 45.66, for succinic acid: 42.84; for malonic acid: 44.24; for oxalic acid: 43.82; and for glutaric acid: 45.14 mN m<sup>-1</sup>. Surface tension of binary mixtures of organic acids with water (20°C < T < 50°C) are calculated as

$$\frac{\sigma_2 - \sigma}{\sigma_2 - \sigma_1} = \left(1 + \frac{ax_2}{1 - bx_2}\right)x_1$$

Table A1

Surface tension parameters  $a$  and  $b$  for aqueous-organic acid mixtures and  $\sigma$  (mN m<sup>-1</sup>) for pure organic (Alvarez et al., 1997)

| Organic acids    | Formic acid |        |          | Acetic acid |        |          | Propionic acid |        |          |
|------------------|-------------|--------|----------|-------------|--------|----------|----------------|--------|----------|
|                  | $A$         | $b$    | $\sigma$ | $a$         | $b$    | $\sigma$ | $a$            | $b$    | $\sigma$ |
| Temperature (°C) |             |        |          |             |        |          |                |        |          |
| 20               | 0.7538      | 0.8442 | 37.58    | 0.7928      | 0.9556 | 27.61    | 0.9103         | 0.9848 | 26.66    |
| 25               | 0.7512      | 0.8457 | 37.03    | 0.7913      | 0.9562 | 27.12    | 0.9096         | 0.9850 | 26.17    |
| 30               | 0.7488      | 0.8473 | 36.47    | 0.7896      | 0.9568 | 26.63    | 0.9089         | 0.9852 | 25.68    |
| 35               | 0.7466      | 0.8488 | 35.94    | 0.7879      | 0.9573 | 26.11    | 0.9081         | 0.9854 | 25.18    |
| 40               | 0.7443      | 0.8504 | 35.39    | 0.7868      | 0.9575 | 25.64    | 0.9073         | 0.9856 | 24.69    |
| 45               | 0.7423      | 0.8521 | 34.87    | 0.7861      | 0.9579 | 25.13    | 0.9066         | 0.9857 | 24.19    |
| 50               | 0.7401      | 0.8536 | 34.34    | 0.7852      | 0.9582 | 24.66    | 0.9058         | 0.9860 | 23.68    |

$\sigma_2 = 72.8$  mN m<sup>-1</sup> surface tensions of pure water,  $a$  and  $b$  are the fitted parameters which depend on the temperature and organic acids (Table A1).

The surface tension of pure formic acid, acetic acid and propionic acid are measured at 298 K to be 37.03, 27.12, 26.17 mN m<sup>-1</sup>, respectively. Since there is no experimental data for all DCA, the surface tension of formic acid is close to that of DCA, and consequently for the temperature of 298.15 K,  $a = 0.7512$ ,  $b = 0.8457$  are estimated.

### A.4. van't Hoff factor

We calculated the van't Hoff factor according to the following equation:

$$a(M) = \frac{m_w}{m_w + im_s \left(\frac{M_w}{M_s}\right)}$$

The original publication is available at [www.doi.org/10.1051/jp4:20030242](http://www.doi.org/10.1051/jp4:20030242).

<https://www.sciencedirect.com/science/article/pii/S135223100500498X>

We also used a fitting formula of variation of water activity with the change of molality for organic acids, using the observed data by Maffia and Meirelles (2001). These fitting equations are:

Molanic acid:  $a=1.0-0.09235237602X-0.3184809942X^2-0.3779219169X^3$

Succinic acid:  $a=1.0-0.2406432307X+0.5844087129X^2-0.9040200495X^3-0.3017637322X^4$ .

Oxalic acid:  $a=1.0-0.9745594766X+13.38641982X^2-92.38641912X^3+293.4885007X^4-$

$478.8562275X^5+388.1267563X^6-123.7935605X^7$ .

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