

A modeling study of aqueous production of dicarboxylic acids: 2. Implications for cloud microphysics

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[1] We estimate the effect of selected small organic species, present in aerosol particles as internal mixtures with sulphate, on cloud microphysical properties using a numerical model. The initial aerosol compositions were motivated by a prior model study in which it was shown that under certain conditions, small dicarboxylic acids, primarily oxalic and glutaric acids, can be efficiently formed via aqueous chemical processes in clouds and remain in the aerosol fraction upon drop evaporation. The simulations performed here separate the effects of the growth in particle mass via in-cloud oxidation from the change in composition of the resulting aerosol. Although the sulphate/organic mixed particles are somewhat less hygroscopic than pure ammonium sulphate, their activity as cloud condensation nuclei in a simulated constant updraft is similar, and the main influence of prior cloud processing of particles arises from the change in total mass and size distribution. We also performed a separate series of simulations initialized with an aerosol consisting of 90% adipic acid/10% ammonium sulphate, chosen to represent a lower limit on the mixed-particle hygroscopic behavior. If only the reduced solubility of the mixture, relative to that of pure sulphate aerosol, is considered, the drop number concentration is suppressed by up to 50%, depending on the choice of initial conditions. However, the suppression of surface tension due to the presence of the organics, modeled using two different approaches, leads to a compensating effect that can result in little net change to the drop concentration relative to that for the pure sulphate aerosol. INDEX

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1. Introduction

[2] Many field, model, and laboratory studies have addressed the interactions between aerosol particles and cloud droplets with a focus on the role of organic compounds. Observations have revealed that at a remote site more than 60% of all cloud condensation nuclei (CCN) can consist of organics [Novakov and Penner, 1993]. In SO₂ and VOC-rich environments organic constituents might also lead to significantly higher particle growth than that predicted by contributions of sulphate alone [Brock et al., 2003]. Observations show that dicarboxylic acids are commonly found in the organic fraction of secondary aerosols

[Grosjean et al., 1978; Kawamura and Ikushima, 1993; Mochida et al., 2003].

[3] As a result, several recent laboratory studies have focused on the investigation of the hygroscopic behavior of dicarboxylic acids or their internal mixtures with inorganics (such as ammonium sulphate) [e.g., Prenni et al., 2001, 2003]. In general it has been found that the solubility of the organics is an important factor in determining the CCN efficiency [e.g., Hegg et al., 2001; Hori et al., 2003]. The CCN efficiency of oxalic, malonic, and glutaric acids, the most abundant dicarboxylic acids in secondary aerosols, is similar to that of ammonium sulphate [Cruz and Pandis, 1997; Giebl et al., 2002; Raymond and Pandis, 2002]. High amounts in, or coatings of glutaric acid on, aerosol particles might even increase the CCN efficiency of pure ammonium sulphate particles [Cruz and Pandis, 1998]. The water uptake of highly soluble species, such as glutaric acid, can be predicted by the Köhler equation, which describes the equilibrium size of an aerosol particle under ambient conditions. Corrigan and Novakov [1999] show that the Köhler equation can be applied for single component organic particles consisting of species with a solubility of >0.5 mol L⁻¹, which is fulfilled for all C₂-C₅ dicarboxylic acids (Figure 1). Particles consisting of less soluble species,

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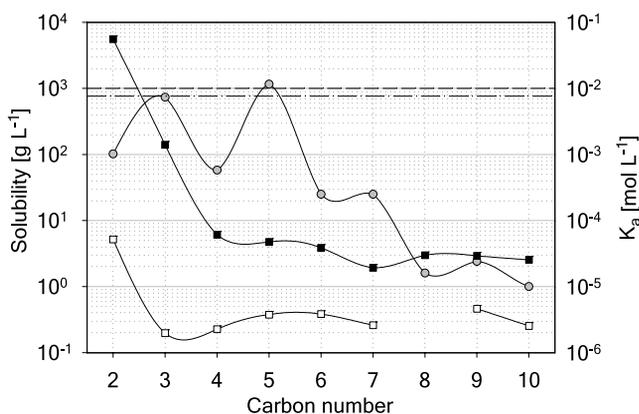


Figure 1. Solubilities in water [g L^{-1}] [Prenni *et al.*, 2001] and acid dissociation constants [M^{-1}] for C_2 – C_{10} (unsubstituted) dicarboxylic acids [Lide, 2000]. Solid circles, solubility; solid squares, $K_a(1)$; open squares, $K_a(2)$; dot-dashed line, solubility of $(\text{NH}_4)_2\text{SO}_4$; dashed line, solubility of NH_4HSO_4 .

such as adipic acid (solubility: $25 \text{ g L}^{-1} = 0.17 \text{ mol L}^{-1}$) do not take up water to a significant extent at relative humidities less than 100% [Prenni *et al.*, 2001; Raymond and Pandis, 2002; Broekhuizen *et al.*, 2004]. Particles composed of species with solubilities less than 10 g L^{-1} do not exhibit appreciable water uptake under typical atmospheric conditions [Shantz *et al.*, 2003].

[4] While most of the previously mentioned studies focused on pure organic aerosols, atmospheric aerosols usually exhibit an internal mixture of ammonium sulphate and organics [Lee *et al.*, 2002]. Brooks *et al.* [2002] showed that mixtures of ammonium sulphate and moderately soluble organics do not significantly alter the deliquescence relative humidity; however, mixtures with maleic acid (solubility 80.4 g L^{-1} [Saxena and Hildemann, 1996]) might be already liquid at very low relative humidities [Brooks *et al.*, 2003]. Recently, it has been shown that the addition of 1% sodium chloride to an organic aerosol particle (leucine, solubility: 8.8 – 9.7 g L^{-1}) leads to a significant decrease in its activation diameter [Raymond and Pandis, 2003], i.e., an increase in its efficiency as a CCN. Figure 1 shows that the short chain acids are much more soluble than the long chain acids. Higher molecular weight acids are less soluble, so they contribute less to the dissolved mass and therefore are unlikely to contribute to growth.

[5] Besides solubility, the acid strength also influences hygroscopic behavior. In the Köhler equation, the degree of dissociation is expressed by the van't Hoff factor ν . While for ionic compounds in dilute solutions this factor is assumed equivalent to the number of the ions [Pruppacher and Klett, 1997], the dissociation of organic acids depends on their acid dissociation constants. The first and second dissociation constants of dicarboxylic acids decrease with increasing carbon number and approach a value of $K_a \approx 10^{-5}$ (Figure 1). Thus these acids are not dissociated in moderately acidic solutions and their van't Hoff factor is usually assumed to be $\nu = 1$ [e.g., Raymond and Pandis, 2002]. An exception is oxalic acid, which might be disso-

ciated in dilute solutions leading to a van't Hoff factor in the range of $1 < \nu < 2$ [Kumar *et al.*, 2003].

[6] In addition to their influence on the amount of mass in solution, organics might also change the surface tension of the particles. It has been shown that this effect might be small for short-chain mono- and dicarboxylic acids [Shulman *et al.*, 1996] but is more distinct in the presence of high molecular weight acids with many functional groups [Facchini *et al.*, 2000; Hitzenberger *et al.*, 2002]. These compounds reduce the surface tension, leading to enhanced drop growth rates [Gorbunov *et al.*, 1998; Nenes *et al.*, 2002]. Broekhuizen *et al.* [2004] showed experimentally that small amounts of surface active species can dramatically enhance the CCN activity of adipic acid particles. On the other hand, the presence of hydrophobic organic films on the surface of particles might suppress particle growth by delaying water vapor uptake [Rudich, 2003, and references therein].

[7] In our previous model study [Ervens *et al.*, 2004] (hereinafter referred to as part 1), we used a cloud parcel model coupled to an aqueous chemistry model to show that small dicarboxylic acids ($\leq \text{C}_6$) can be efficiently formed by chemical processes in clouds. In a clean continental case, it is predicted that an internally mixed sulphate/organic aerosol with significant organic mass fraction results from cloud processing of the input aerosol which was composed of pure ammonium sulphate. (Initial concentrations: $[\text{SO}_2]_0 = 0.01 \text{ ppb}$, $[\text{NO}_x]_0 = 0.05 \text{ ppb}$, $[\text{toluene}]_0 = 0.01 \text{ ppb}$, $[\text{ethene}]_0 = 0.1 \text{ ppb}$, $[\text{cyclohexene}]_0 = 0.05 \text{ ppb}$, $[\text{isoprene}]_0 = 2 \text{ ppb}$, and $N_a = 100 \text{ cm}^{-3}$). For polluted conditions, in-cloud sulphate production exceeds organic production, and the contributions of dicarboxylic acids produced in clouds to total aerosol mass are on the order of only a few percent. Therefore we focus on clean continental conditions and do not investigate composition effects in polluted conditions. In the present study we initialize the model with cloud processed aerosols the composition of which is based on the aqueous chemistry mechanism presented in part 1. First, we consider the extent to which the additional mass and the modified aerosol composition resulting from cloud processing influence cloud microphysics in subsequent cloud cycles. The study uses a detailed description of the aerosol/cloud microphysics but does not include any gas or aqueous chemical processes. In addition to the effects of mass and composition, we investigate the influence of different updraft velocities, and also consider two different initial aerosol size distributions. In order to give an upper limit for possible effects, we perform additional model studies for particles composed of 90% adipic acid and 10% ammonium sulphate. Finally, we briefly consider the relative roles of composition and surface tension in determining cloud droplet concentrations and sizes.

2. Model

2.1. Description of Microphysical Treatment of Aerosols

[8] In the current study, the cloud parcel model used in part 1 has been modified. In part 1, we were primarily concerned with investigation of complex inorganic and organic multiphase chemistry and the modification of the aerosol composition. The effects of aerosol composition on aerosol/drop growth were neglected. Here we address the

implications of mass and composition modification on droplet activation and growth. Together, these two modeling approaches allow for a differentiation of the effects of cloud chemistry and cloud physics on the complex feedback between aerosol particles and clouds.

[9] In the previous model study, the air parcel was driven by a kinematic trajectory derived from a boundary layer model [Stevens *et al.*, 1996]. The trajectory exposed a parcel of air to a cloud for about 800 s in the hour-long cycle having a maximum water mixing ratio of $\sim 0.3 \text{ g kg}^{-1}$. Here we perform simulations with an adiabatically cooled air parcel rising with a constant updraft velocity until a total liquid water mixing ratio of 0.3 g kg^{-1} is achieved. The initial height of the air parcel is 300 m at a relative humidity of 85% and a temperature of 288.15 K.

[10] The calculation of the water activity of the multi-component inorganic/organic aerosol is performed with a thermodynamic model that is applied to individual particle compositions for each of the ten logarithmically spaced size classes. This model uses as input the molalities [mol kg^{-1}] of the dissolved inorganic (ammonium, sulphate) and organic species (formic, acetic, glycolic, glyoxylic, pyruvic, oxalic, malonic, succinic, glutaric, and adipic acid); no other species, soluble or insoluble, are considered. At each time step the soluble fractions for glyoxylic, oxalic, succinic and adipic acids are calculated using their solubilities in dilute solutions (102 g L^{-1} , 102 g L^{-1} , 88 g L^{-1} , 25 g L^{-1} , respectively) as a threshold for the maximum amount of material in solution. It is assumed that all other aerosol species, including ammonium (bi-)sulphate/sulfuric acid, are always completely dissolved, which is justified since at the initial relative humidity ($\text{RH}_0 = 85\%$) the particles contain some water. The aqueous phase dissociation of the organic acids was calculated using available dissociation constants for 298.15 K. The activity coefficient for each species in solution and the osmotic coefficient of the solution are calculated using the model of Pitzer [1991], which is applicable to relative humidities greater than about 75%, well below the minimum relative humidity considered in these simulations. The activity coefficients of the undissociated acids were assumed to be unity, and those of the acid anions were described by the Debye-Hückel expression within the Pitzer equations. The parameters describing interactions between inorganic ions and all organic species were set to zero. Parameters for aqueous H_2SO_4 were taken from Clegg *et al.* [1994], and those for $(\text{NH}_4)_2\text{SO}_4$ and its mixtures with H_2SO_4 from Clegg *et al.* [1996]. We note that the presence of multiple organic species in the solution acts to suppress the relative humidity at which a saturated solution of each organic will form. Thus the organic species in the particles begin to take up water at slightly lower relative humidities than predicted by considering the effects of individual species independently.

2.2. Description of Simulations

[11] The aqueous production of both sulphate and organic aerosol mass leads to (1) mass addition to the initial aerosol population, and (2) modification to the composition of the initial ammonium sulphate aerosols, and thus to aerosol hygroscopic properties. The size distribution, the organic fraction in each size class, and the composition of the organic fraction in the initial aerosol are shown in Figures 2a–2c.

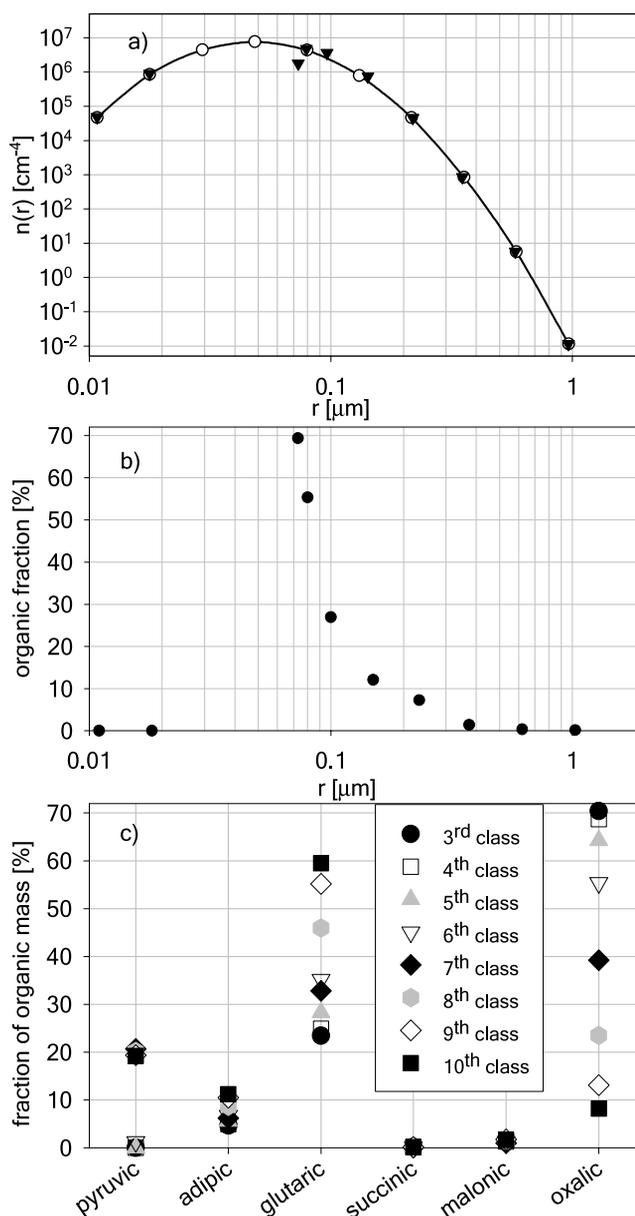


Figure 2. (a) Initial lognormal aerosol size distribution and aerosol size distribution previously processed by eight cloud cycles (open circles, initial aerosol; solid triangles, processed aerosol). (b) Organic fraction in each size class after eight cloud cycles. (c) Composition of the organic fraction.

[12] In the following, we describe the different model runs that allow for a separation of the effects on clouds due to mass addition and composition modification, respectively: For each set of model simulations a base run (I) is performed with an initial lognormal aerosol size distribution comprising pure ammonium sulphate particles (Figure 2). The second (II) simulation addresses the effect of mass addition by aqueous phase production of sulphate and organics. The total aerosol mass, i.e., ammonium sulphate and organics, is treated completely as ammonium sulphate (as in part 1). Run III is initialized with the identical mass distribution as in run II but the water

Table 1. Description of the Different Model Runs

Run	Aerosol Size Distribution	Composition	Comment
I	Lognormal	Ammonium sulphate	'base case'
II	Modified by sulphate/organics mass production in 8 cloud cycles	Ammonium (bi-)sulphate/organics	Total mass treated as ammonium sulphate
III	Modified by sulphate/organics mass production in 8 cloud cycles	Ammonium (bi-)sulphate/organics	Same total mass as II Ammonium, sulphate, and organics are treated explicitly
IV	Modified by sulphate/organics mass production in 8 cloud cycles	90% adipic acid/ 10% ammonium sulphate	Same total mass as II

uptake of the mixture of all twelve aerosol constituents (i.e., ammonium, sulphate, and ten organic acids) is described explicitly. Although Figure 2 shows only the main organic components (namely, the low volatility dicarboxylic acids and pyruvic acid), minor contributions from all the other (monocarboxylic) acids are taken into account in run III.

[13] In order to place bounds on the maximum effect of the organic compounds considered in this study, run IV is initialized with the identical total mass as runs II and III but the total mass is divided into 90% organics/10% ammonium sulphate in each size class. To give an upper limit of the influence of small dicarboxylic acids on the water uptake, a composition of 90% adipic acid and 10% ammonium sulphate is assumed. This latter run is performed since adipic acid has the lowest solubility among the currently considered aerosol constituents and exhibits the largest difference in hygroscopic behavior compared to ammonium sulphate [e.g., Cruz and Pandis, 1997]. A description of these simulations is given in Table 1.

3. Results and Discussion

3.1. Variation of Updraft Velocity

3.1.1. Cloud Processed Aerosol

[14] The number of activated particles depends strongly on the updraft velocity of the air parcel. For a parcel that rises and cools adiabatically, the cooling rate and, hence, the maximum supersaturation, is determined by the updraft velocity w (aerosol conditions being equal). In a model study, Feingold and Kreidenweis [2000] investigated the dependence of the relative change in drop number concentration, N_d , on different updraft velocities for ammonium sulphate aerosol and showed that processing tends to create the largest positive change in N_d at low w . The sensitivity of activation of organic and inorganic aerosols (adipic acid versus ammonium sulphate) to different w was compared by Shantz *et al.* [2003] showing that the dependence of the number of activated particles on w is stronger for organic than for ammonium sulphate particles.

[15] We perform model simulations (I-IV as described in Table 1) using a parcel model with constant w of 200 cm s⁻¹ and 50 cm s⁻¹, respectively. Table 2 summarizes the results for the maximum supersaturation, number of activated size classes, fraction of particles activated (N_d/N_a) and drop effective radius r_e . It should be noted that these model studies consider only ten size classes causing step-like changes in N_d . Supersaturation differences are usually much smaller because of dynamical feedbacks: higher supersaturations result in higher N_d , which tends to reduce supersaturation. We have assumed a threshold of 1 μ m for the

minimum drop radius used to determine total drop number concentrations.

[16] For the first set of entries, there are only minor differences in the drop size spectrum, which is reflected by almost the same r_e for all assumed compositions (Table 2). In order to examine more closely the different droplet growth histories in the various cases studied, the evolution of the radius in the third size class is shown (Figure 3). In this size class both the organic fraction and total mass addition due to cloud processing are highest (Figure 2), so that the most significant changes in the water uptake can be expected there. It is clear that the drop growth on the unprocessed (pure ammonium sulphate) aerosol is delayed (run I) because the size of these particles is much smaller than for class 3 processed particles. However, comparison of the drop growth assuming that the added mass is composed of pure ammonium sulphate and an ammonium sulphate/organic mixture (Figure 2) reveals only marginal delay in growth for the aerosol containing organics (run II/III), i.e., the CCN activity of the additional, mostly organic mass, is similar to that of ammonium sulphate.

[17] The organic fractions in all size classes are mainly composed of oxalic and glutaric acid. Comparison with

Table 2. Summary of the Model Results Assuming Different Updraft Velocities, Initial Size Distributions, and Compositions

Run	Initial Size Distribution	w , cm s ⁻¹	Number of Activated Size Classes	S_{\max} , %	r_e , μ m	N_d/N_a , %
I	$r_g = 0.06$, $\sigma = 1.6$	200	9	1.3	8.0	98
II	processed by clouds	200	9	1.3	8.0	98
III	processed by clouds	200	9	1.3	8.0	98
IV	processed by clouds	200	8	1.3	8.1	96
I	$r_g = 0.06$, $\sigma = 1.6$	50	8	0.6	8.0	96
II	processed by clouds	50	8	0.5	8.0	96
III	processed by clouds	50	8	0.5	8.0	96
IV	processed by clouds	50	8	0.6	8.0	96
I	$r_g = 0.06$, $\sigma = 1.6$	10	7	0.2	8.4	85
IV	$r_g = 0.06$, $\sigma = 1.6$	10	6	0.4	12.2	47
I	$r_g = 0.04$; $\sigma = 2$	200	9	1.4	8.1	92
IV	$r_g = 0.04$; $\sigma = 2$	200	8	1.6	8.5	78
I	$r_g = 0.04$; $\sigma = 2$	100	9	0.9	8.2	92
IV	$r_g = 0.04$; $\sigma = 2$	100	7	1.1	9.8	53
I	$r_g = 0.04$; $\sigma = 2$	10	7	0.3	9.8	53
IV	$r_g = 0.04$; $\sigma = 2$	10	6	0.4	12.4	26
<i>20 Size Classes</i>						
I	$r_g = 0.04$; $\sigma = 2$	200	18	1.4	8.1	95
IV	$r_g = 0.04$; $\sigma = 2$	200	16	1.6	8.6	81
I	$r_g = 0.04$; $\sigma = 2$	100	17	0.9	8.3	90
IV	$r_g = 0.04$; $\sigma = 2$	100	15	1.1	9.1	69
I	$r_g = 0.04$; $\sigma = 2$	10	14	0.3	9.6	56
IV	$r_g = 0.04$; $\sigma = 2$	10	12	0.4	12.2	28

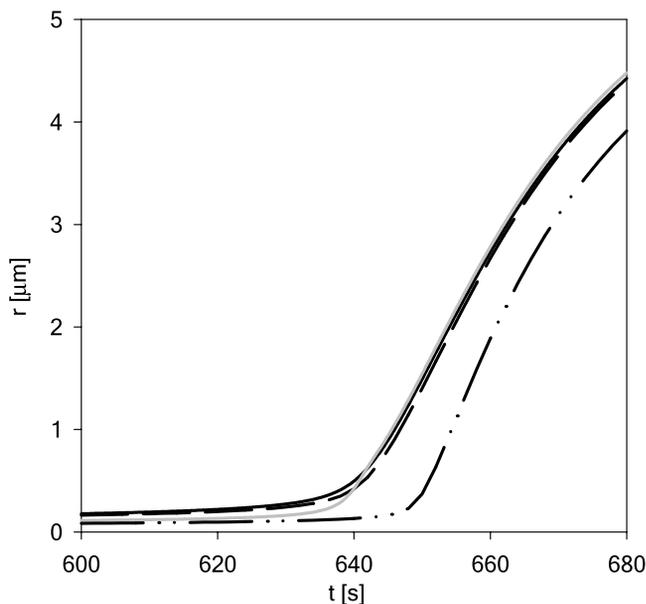


Figure 3. Evolution of drop radius in the third size class (processed by clouds; initial radius $r_{dry} = 0.07 \mu\text{m}$); $w = 50 \text{ cm s}^{-1}$. Dot-dashed line, initial lognormal size distribution (run I); solid black line, pure ammonium sulphate (run II); dashed line, sulphate/organic mixture (cloud processed) (run III); solid gray, 90% adipic acid/10% ammonium sulphate (run IV).

laboratory measurements of the CCN efficiency of these highly soluble acids shows that the growth factors of an internal mixture of 40% oxalic acid/60% ammonium sulphate or 40% glutaric acid/60% ammonium sulphate differ negligibly, or are reduced by 12%, respectively, compared to pure ammonium sulphate (at $\text{RH} = 90\%$, $r_{dry} = 100 \text{ nm}$) [Prezzi *et al.*, 2003]. A distinct change in hygroscopic behavior caused by the presence of small dicarboxylic acids might only be expected if the organic fraction is both quite high and much less soluble, as assumed for run IV. Figure 3 shows that the growth in this size class for run IV is not significantly different than that for the other assumed cases. However, it should be kept in mind that this latter composition (run IV) does not correspond to the different organic fractions as shown in Figure 2b but to a constant organic (adipic acid) fraction of 90% in each size class. This leads to smaller growth rates for all particles and a higher supersaturation builds up which favors the growth of smaller particles (e.g., third class). Thus the growth rate for run IV shown in Figure 3 is a result of two compensating effects: (1) a reduction due to the higher undissolved fraction compared to run III but (2) an increase due to the higher supersaturation which is caused by the large undissolved fraction in the particles.

[18] In Figure 4 a time series of the fraction of particles activated (N_d/N_a) is shown for runs II, III, and IV at constant updraft velocities of $w = 50 \text{ cm s}^{-1}$ and $w = 200 \text{ cm s}^{-1}$, respectively. The pure ammonium sulphate particles and the particles containing the complex ammonium sulphate/organic mixture exhibit almost exactly the same growth as reflected in the simultaneous increase in N_d/N_a . It is noted again that this step-like increase of drop number is at least

partially due to the relatively low size resolution in these simulations. The growth of the particles that contain high fractions of adipic acid is clearly delayed in the first part of the simulation period. However, at the end of the simulation all lines converge. Thus the less soluble material causes a delay in growth in the earlier stages of the cloud formation, i.e., at very low liquid water contents ($\text{LWC} \sim 0.01 \text{ g kg}^{-1}$). As the amount of water increases and the adipic acid mass is gradually dissolved, its hygroscopic behavior becomes similar to that of highly soluble inorganic or organic material. This qualitative behavior can be seen for both updraft velocities. However, the delay in growth caused by the less soluble organic acid is less significant at the higher w . This delay in the drop number evolution occurs over a short period of time (a few tens of seconds, or heights above cloud base on the order of a few tens of meters).

[19] We can conclude that, based on the selected simulation conditions, neither the changes in the size distribution

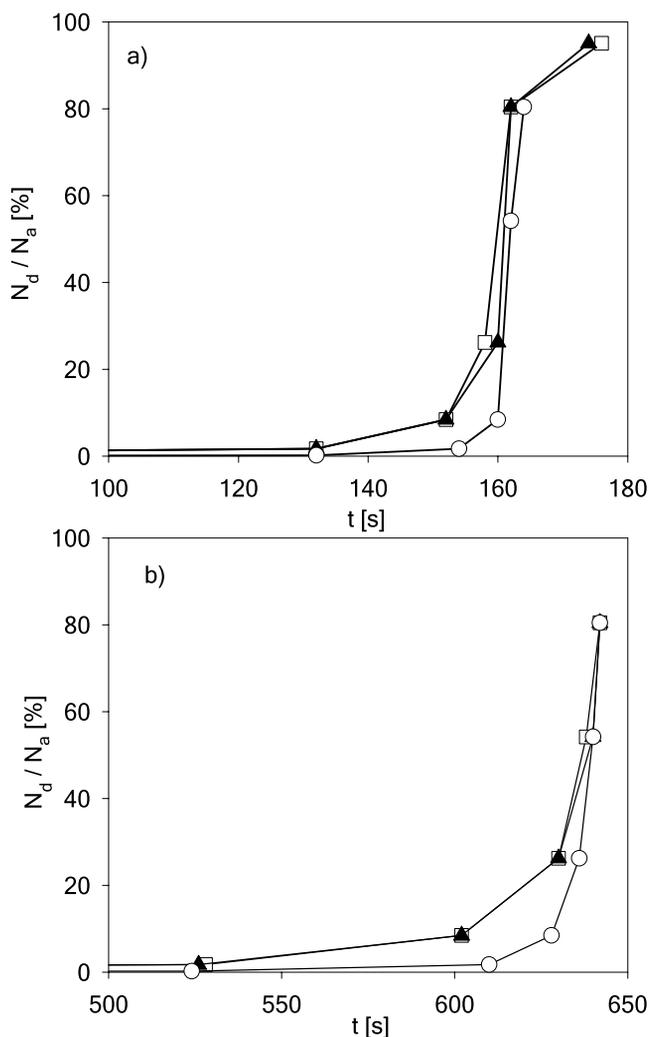


Figure 4. Time series of evolution of relative fraction of particles activated (N_d/N_a) (for the cloud processed aerosol size distribution). Open squares, ammonium sulphate (run II); solid triangles, sulphate/organic mixture (cloud processed) (run III); open circles, 90% adipic acid/10% ammonium sulphate (run IV). (a) $w = 200 \text{ cm s}^{-1}$; (b) $w = 50 \text{ cm s}^{-1}$.

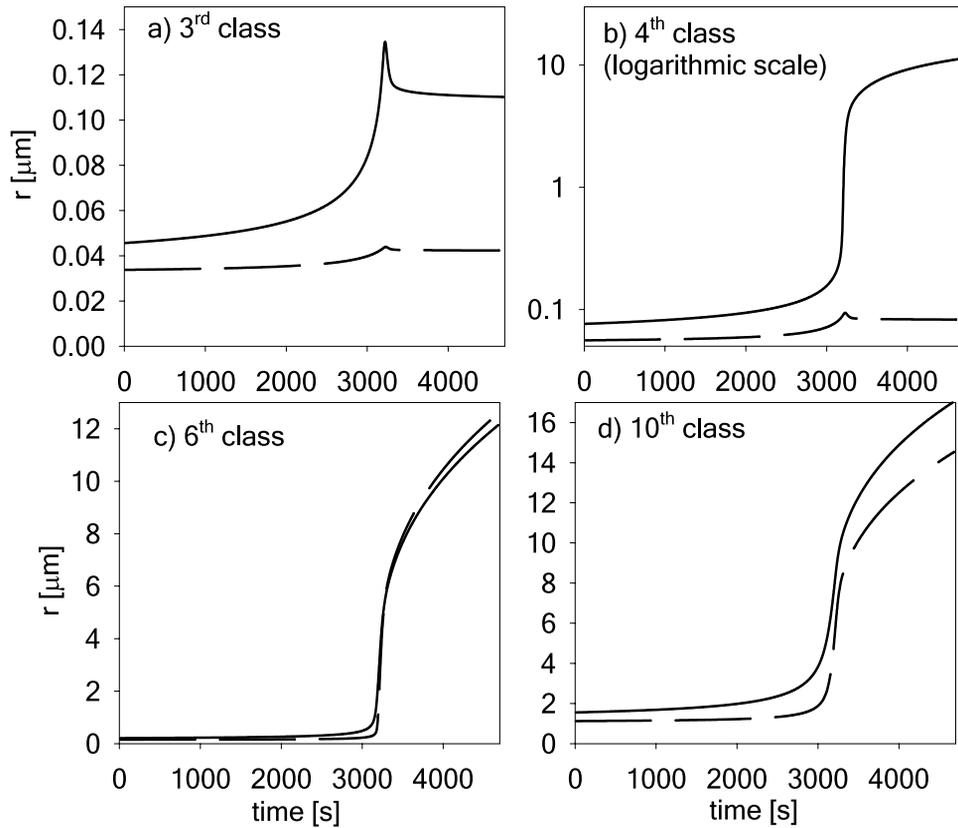


Figure 5. Drop radii [μm] in the (a) third, (b) fourth, (c) sixth, and (d) tenth size classes. Initial aerosol size distribution: lognormal $r_g = 0.06 \mu\text{m}$, $\sigma = 2$, $w = 10 \text{ cm s}^{-1}$. Solid line, pure ammonium sulphate (run II); dashed line, 90% adipic acid/10% ammonium sulphate (run IV).

(Figure 2a) nor the composition modification (Figures 2b and 2c) due to cloud processing seem to be sufficient to influence the microphysical behavior of the particles, as reflected by N_d and r_e . Higher resolution of the size distribution into 20 size classes does not change this conclusion significantly (see section 3.3). The only marked differences we could find were for particles with high fractions of less soluble acids, e.g., adipic acid. Therefore, in the following sections, we focus on a comparison between particles composed largely of the less soluble organics and particles composed of pure ammonium sulphate.

3.1.2. Lognormal Aerosol Size Spectrum

[20] Model studies often use parameterizations such as lognormal functions to represent aerosol size distributions. In order to facilitate a comparison of our model to these model studies, we investigate the extent to which composition might influence drop size distribution and N_d for prescribed lognormal size distributions, and for different w . We use the lognormal size distribution as applied in run I ($r_g = 0.06 \mu\text{m}$ and $\sigma = 1.6$, $N_a = 100 \text{ cm}^{-3}$, pure ammonium sulphate) and compare the results with those obtained from model runs assuming 90% adipic acid/10% ammonium sulphate with the identical total mass and an initial lognormal size distribution.

[21] Results for an updraft velocity of $w = 200 \text{ cm s}^{-1}$ show that even a high fraction of adipic acid results in negligible increase in r_e ($\sim 1\%$) compared to pure ammonium sulphate.

At this high updraft velocity, almost all particles (eight or nine of the ten size classes, respectively) grow to drop sizes, so there is no significant change in N_d between the cases. The same model runs were also performed for a much lower w ($= 10 \text{ cm s}^{-1}$, Table 2) where we find a significant reduction in activated fraction compared to the results for ammonium sulphate (85% versus 47%). As expected, the maximum supersaturation is significantly lower compared to that computed at higher w for both compositions. Only particles with dry radii $r_{dry} \geq 0.08 \mu\text{m}$ (pure ammonium sulphate) and $r_{dry} \geq 0.05 \mu\text{m}$ (90% adipic acid/10% ammonium sulphate), respectively, reach the assumed minimum drop size of $1 \mu\text{m}$. In Figure 5 it can be seen that the large drops (tenth size class) containing adipic acid are significantly smaller than those formed on pure ammonium sulphate aerosols, while the drops in the sixth class are larger. The enhanced water uptake by the significant particle number in the sixth size class ($N_a = 35 \text{ cm}^{-3}$) causes a distinct suppression of the growth rates in the smaller size classes, and as a result the fourth size class in the 90% adipic acid/10% ammonium sulphate case grows to droplet sizes. The concentration in the fourth size class is $N_a = 37 \text{ cm}^{-3}$, so that in the case of the adipic acid/ammonium sulphate particles, roughly 40% fewer drops are formed compared to the results for pure ammonium sulphate (85 cm^{-3} versus 47 cm^{-3}), resulting in an increase in r_e of about 50%. As shown in section 3.3, these numbers may change if a higher resolution of the size classes is considered.

[22] In general, our results are in good agreement with findings by *Shantz et al.* [2003]. They find that the number of activated particles is reduced by about 5% for pure ammonium sulphate and 55% for pure adipic acid particles, respectively, if the updraft velocity is lowered from 50 cm s^{-1} to 20 cm s^{-1} . Their values may represent an upper bound for the composition effects since they consider pure adipic acid particles. Their results may also be sensitive to size resolution.

3.1.3. Variation of Initial Lognormal Aerosol Size Distribution

[23] The shape of the initial aerosol size distribution can have a significant influence on the fraction of activated particles [*Feingold and Kreidenweis, 2000; Kreidenweis et al., 2003*]. The combination of aerosol size distribution parameters, updraft velocity, location of the minimum activated aerosol size relative to the size distribution, as well as the size resolution in the vicinity of this minimum size, all determine the activation response and the sensitivity to changes due, e.g., to composition. In order to explore the influence of different initial size distributions, we change the lognormal parameters to $r_g = 0.04 \text{ }\mu\text{m}$ and $\sigma = 2$ (compared to $r_g = 0.06 \text{ }\mu\text{m}$, $\sigma = 1.6$ in section 3.1.2).

[24] Results from runs I and IV should clarify if for this initial aerosol size spectrum different aerosol compositions lead to different drop size distributions since each simulation uses the identical mass concentration and lognormal size distribution. Both runs are performed for constant w of 200 cm s^{-1} . Comparison of results from run I (pure ammonium sulphate) and run IV (90% adipic acid/10% ammonium sulphate) reveals that over the range of updraft velocities investigated here, both r_e and S_{max} are increased significantly in the latter case. The same number of size classes grows to drop sizes (eight or nine, respectively) as for the previous lognormal size distribution ($r_g = 0.06 \text{ }\mu\text{m}$, $\sigma = 1.6$). While previously this difference caused a change in the drop number of only about $\Delta N_d \sim 2\%$, the relative change in drop number is now $\Delta N_d \sim 14\%$.

[25] A more detailed picture of the dependence of the drop number on the updraft velocities is obtained by applying updraft velocities of 10 cm s^{-1} and 100 cm s^{-1} for runs I and IV (Table 2). At $w = 100 \text{ cm s}^{-1}$, nine size classes grow to drops if pure ammonium sulphate particles are considered. However, for 90% adipic acid/10% ammonium sulphate aerosol, the growth rate of the third size class is significantly suppressed resulting in a significant decrease in N_d ($\Delta N_d \sim 40\%$). At low w (10 cm s^{-1}) ΔN_d is about 50%.

3.2. Can the Results Be Generalized?

[26] In the previous sections we presented results showing influences of different initial size distributions and updraft velocities. However, these results permit only a restricted interpretation of the influence of variation of these parameters and a limited set of conclusions. In this section we seek common trends reflected in the predictions initialized with the different size distributions and variations in w . These trends help identify a more general parameter space in which the composition of particles and, in particular, high fractions of moderately soluble organic species might influence the cloud microphysical response to aerosol populations.

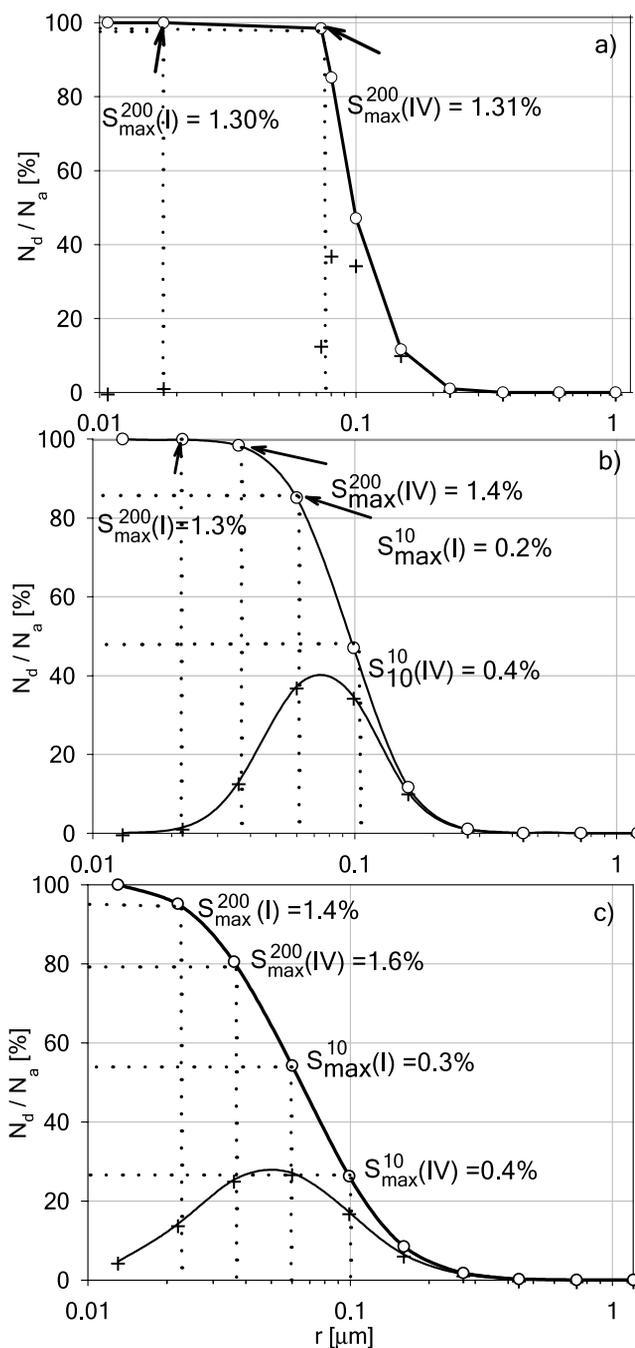


Figure 6. Particle number concentration (pluses) and cumulative number concentration (open circles) as a function of radius [μm]. (a) Cloud processed size distribution; (b) lognormal size distribution ($r_g = 0.06 \text{ }\mu\text{m}$, $\sigma = 1.6$); (c) lognormal size distribution ($r_g = 0.04 \text{ }\mu\text{m}$, $\sigma = 2$). $S_{\text{max}}(\text{I})$ and $S_{\text{max}}(\text{IV})$ refer to the maximum supersaturations achieved at an updraft velocity $w = 200 \text{ cm s}^{-1}$ and $w = 10 \text{ cm s}^{-1}$ for pure ammonium sulphate (I) and adipic acid/ammonium sulphate particles (IV), respectively.

[27] In Figure 6, three initial size distributions are shown: processed by clouds (part 1) (Figure 6a), $r_g = 0.06 \text{ }\mu\text{m}$, $\sigma = 1.6$ (Figure 6b), and $r_g = 0.04 \text{ }\mu\text{m}$, $\sigma = 2$ (Figure 6c). All three size distributions have $N_a = 100 \text{ cm}^{-3}$. The location of the minimum activated class and S_{max} for $w = 200 \text{ cm s}^{-1}$

are indicated. As shown in section 3.1.1, the composition changes lead to an absolute difference of one drop size class in these simulations. For Figures 6a and 6b the dry radius of this minimum activated size class is quite small and located in a relatively flat part of the cumulative aerosol number concentration curve. Thus the change in N_d is not very significant. This is not the case in Figure 6c, where we see that a small difference in S_{\max} due to the composition change results in a fairly large change in N_d (92 cm^{-3} versus 78 cm^{-3} ; Table 2) because S_{\max} is located on a fairly steep section of the cumulative aerosol concentration curve.

[28] The relative change in N_d is much more significant (Table 2) at $w = 10 \text{ cm s}^{-1}$ since the slope of the cumulative particle number concentration is much steeper. Lower updraft velocities also mean that large particles are able to reach sizes closer to their equilibrium sizes during the initial stages of their growth in subsaturated conditions. If they exist in large enough concentrations, this too can result in lower supersaturations. The smallest activated size class contains a significant fraction of N_a , so that even small changes in supersaturation might cause a significant change in N_d .

[29] Figure 6 reveals that the relative change in N_d due to composition change depends on (1) the shape of the aerosol size distribution, and (2) the maximum supersaturation that is achieved in the cloud parcel and its position, and the minimum activated particles size relative to the mode of the aerosol size distribution. Organic contributions to aerosol mass will exhibit the strongest effect on cloud drop number concentrations if the smallest size class that can grow to drop size is located near the maximum of the size spectrum.

3.3. Increase in Size Resolution

[30] As discussed above, it is difficult to generalize the relative changes in N_d and the feedback to the supersaturation since they are strongly dependent on the number of particles in each size class, the size of the smallest activated size class and on the size resolution. In order to assess whether we overestimate the relative change in N_d due to composition change, we perform a few selected runs with a size resolution of 20 size classes. The same lognormal size distribution as in section 3.1.3 is used ($r_g = 0.04 \mu\text{m}$, $\sigma = 2$). Values for N_d , r_{es} and S_{\max} are summarized in Table 2. The relative effect on composition N_d at the lowest ($w = 10 \text{ cm s}^{-1}$) and highest ($w = 200 \text{ cm s}^{-1}$) updraft velocities is quite similar ($\Delta N_d = 50\%$ and $\Delta N_d = 15\%$, respectively), although absolute drop numbers are slightly different compared to the drop number concentrations that result from resolution in ten size classes. However, results at $w = 100 \text{ cm s}^{-1}$ illustrate that the change in resolution may lead to differences for this example. N_d is most sensitive updraft velocity if the size of the smallest activated size class is located near the maximum of the aerosol size distribution (3.2). For the size distribution under discussion this maximum is located at the fourth size class. If the size resolution is higher, the supersaturation is sufficient to activate particles with sizes that are slightly larger, which causes a significant change in N_d given the proximity of the mode size.

3.4. Effects of Surface Tension

[31] In the previous sections we focused on the effects of gradually dissolving organic aerosol mass during drop

growth. However, we neglected the effect of the organic compounds on the surface tension, which is represented in the second term on the right-hand side of the droplet growth equation:

$$r \frac{dr}{dt} \propto S - \exp\left(\frac{A}{r} - \frac{B}{r^3}\right), \quad (1)$$

where S is the supersaturation, r is the particle radius, A is a function of surface tension $\sigma_{w,s}$, and B is a function of the soluble mass and its composition.

[32] The surface tension $\sigma_{w,s}$ of an ammonium sulphate solution is larger than that for pure water (σ_w) [Pruppacher and Klett, 1997] and can be calculated as

$$\sigma_{w,s} = \sigma_w + 2.17 \cdot [(\text{NH}_4)_2\text{SO}_4], \quad (2)$$

where $[(\text{NH}_4)_2\text{SO}_4]$ is the molality of ammonium sulphate [mol kg^{-1}]. On the other hand, water-soluble organics can decrease the surface tension of aqueous droplets. An empirical relation between the surface tension suppression and the concentration of organic acids in water c_{org} [mol L^{-1}] is given by [Langmuir, 1917]

$$\sigma_{w,s} = \sigma_w \cdot \left(1 - b \cdot \log_{10}\left(\frac{c_{\text{org}}}{a} + 1\right)\right), \quad (3)$$

where a and b are compound-specific constants. *Facchini et al.* [1999] measured the surface tension of fog samples containing a complex mixture of organic and inorganic compounds. They fitted their results to the equation by Langmuir (equation (3)) using the dissolved organic carbon concentration instead of the concentration of specific organic compounds, and thus obtained the following equation:

$$\sigma_{w,s} = 72.8 - 0.01877 \cdot T \cdot \ln(1 + 628.14 \cdot [C]), \quad (4)$$

where T is the temperature [K] and $[C]$ is the concentration of the water-soluble organic carbon (WSOC) [mol L^{-1}]. This equation (equation (4)) has been used in model studies in order to investigate the effect of dissolved organics on particle activation. It has been shown that under certain conditions, the lowering of the surface tension can lead to a significant increase in the drop number concentration [Facchini et al., 2000; Anttila and Kerminen, 2002; Rissman et al., 2004].

[33] In order to compare results from these previous model studies to our present model, we replace the description of the surface tension (2) used in the earlier simulations reported here by (4). The carbon concentration for the respective organic compounds, $[C]$, was obtained by multiplying the concentration of the dissolved acid by the number of carbon atoms. In addition to the composition used in the previous section (90% adipic acid/10% ammonium sulphate), we also compare results for an aerosol composed of 90% glutaric acid/10% ammonium sulphate. Glutaric acid represents the most soluble dicarboxylic acid considered in the model, and thus its total mass always contributes to both terms in (1). Results for model runs are summarized in Table 3 for three different updraft velocities (10 cm s^{-1} , 100 cm s^{-1} , and 200 cm s^{-1}) and using an

Table 3. Effects of Surface Tension Changes on r_e and N_d/N_a Due to Different Approaches and Compositions

	Surface Tension	$w = 200 \text{ cm s}^{-1}$		$w = 100 \text{ cm s}^{-1}$		$w = 10 \text{ cm s}^{-1}$	
		$r_e, \mu\text{m}$	$N_d/N_a, \%$	$r_e, \mu\text{m}$	$N_d/N_a, \%$	$r_e, \mu\text{m}$	$N_d/N_a, \%$
Pure ammonium sulphate	$f((\text{NH}_4)_2\text{SO}_4)$	8.2	92	8.2	92	9.8	53
90% adipic acid/ 10% ammonium sulphate	$f((\text{NH}_4)_2\text{SO}_4)$	8.7	78	9.8	53	12.4	26
90% adipic acid/ 10% ammonium sulphate	$f([\text{adipic acid}])$	8.2	92	8.2	92	9.7	53
90% glutaric acid/ 10% ammonium sulphate	$f([\text{glutaric acid}])$	8.0	100	8.1	92	9.8	53

initial lognormal size distribution ($r_g = 0.04 \mu\text{m}$, $\sigma = 2$, $N_a = 100 \text{ cm}^{-3}$). The results in Table 3 reveal that the suppression of surface tension might compensate for the reduced drop number concentration due to a decreased solubility so that almost the same number of drops is formed as in the case of pure ammonium sulphate. Results of these selected cases suggest that surface tension effects and the solubility of organics compete with one another by simultaneously decreasing the Kelvin term (A/r) and the Raoult term (B/r^3).

[34] Equation (4) was obtained by fitting data from real cloud and fog water and represents an empirical relation for the net effect of carbonaceous species on the surface tension of droplets containing a complex mixture of poly-, di-, and monocarboxylic acids, in addition to various dissolved inorganic species. However, it is likely to be an overestimate of surface tension lowering for this study, since as *Facchini et al.* [2000] show, most of the surface tension reduction that they observed was due to larger molecules not considered in this work. The effects of individual small dicarboxylic acids on surface tension of aqueous solutions were experimentally determined by *Shulman et al.* [1996]. Fitting their data to (3), we obtain the following constants a and b for glutaric and adipic acid, respectively:

$$\text{glutaric acid : } a = 0.149 \pm 0.044; b = 0.215 \pm 0.026; r^2 = 0.991; n = 6$$

$$\text{adipic acid : } a = 0.019 \pm 0.017; b = 0.105 \pm 0.044; r^2 = 0.960; n = 4.$$

[35] In Figure 7 both the experimental data by *Shulman et al.* [1996] and the fitting results using the coefficients above are shown. In addition, the values for the surface tension that are derived from (4) assuming glutaric and adipic acid, respectively, as contributions to the concentration term [C] are included. For these particular species the surface tension suppression is greatly overestimated by (4).

[36] Table 3 shows that the relative differences in N_d and r_e due to surface tension effects are almost independent of the updraft velocity. Figure 8 shows that the time series of the evolution of the activated particle fraction is similar for an updraft velocity of 200 cm s^{-1} . It is evident that consideration of the surface tension lowering by organics leads to an accelerated particle activation leading finally to an increase in N_d in the cases considered here.

[37] In order to focus on differences in N_d and r_e caused by the different descriptions of the surface tension, we performed additional model runs for 20 size classes using an updraft velocity of $w = 200 \text{ cm s}^{-1}$. The results are summarized in Table 4 for both mixture compositions. It is seen again that neglecting the surface tension suppression by organics leads to an underestimate of N_d and thus to

effective radii that are too large. However, the use of the empirical equation by *Facchini et al.* [1999] (equation (4)) yields an overestimate of N_d compared to the more appropriate estimates of solution surface tension that we have developed in the current study for glutaric and adipic acids.

4. Conclusions and Future Outlook

[38] In many studies it has been shown that the presence of organics might influence and modify the hygroscopic

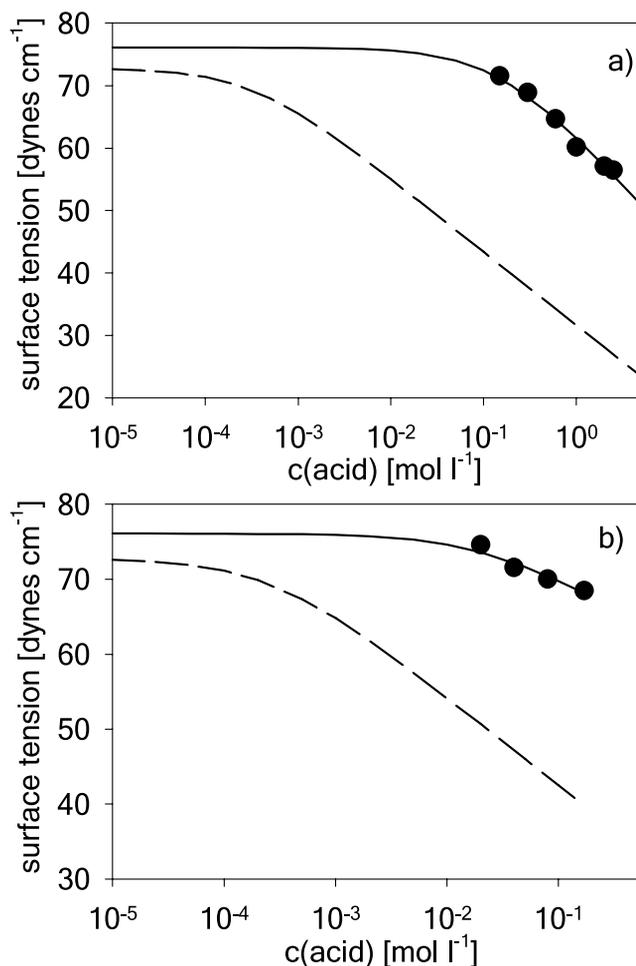


Figure 7. Dependence of surface tension for (a) glutaric acid and (b) adipic acid. Dashed line, results derived by using equation by *Facchini et al.* [1999] (equation (4)); solid circles, measured data by *Shulman et al.* [1996]; solid line, fitting results using equation by *Langmuir* [1917] (equation (3)). Note: The maximum solubility of adipic acid in water is 0.17 M.

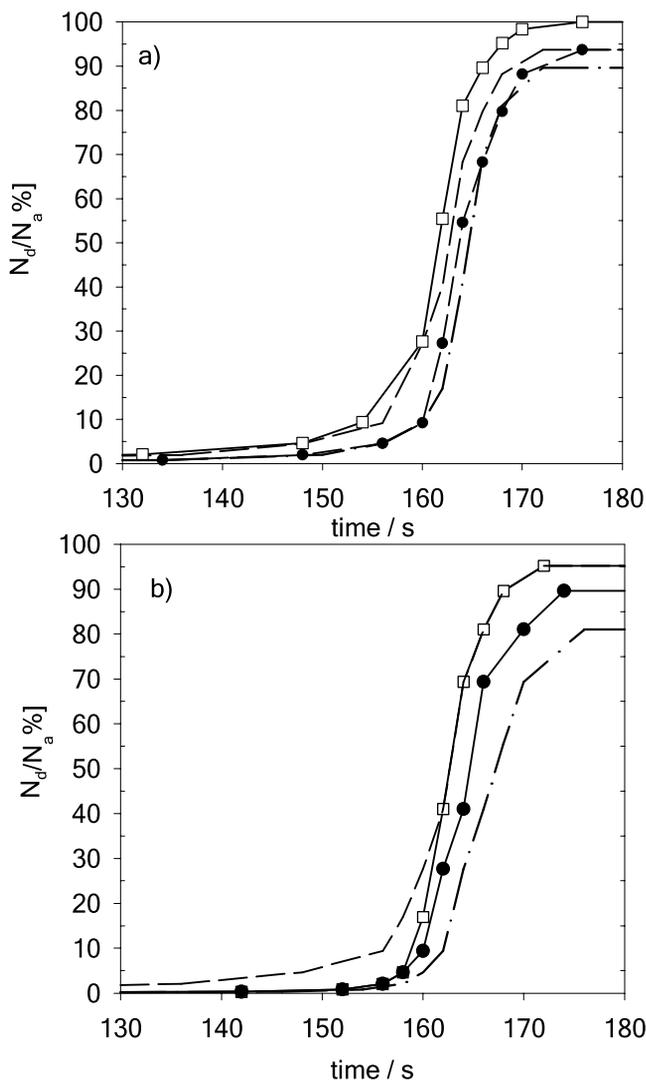


Figure 8. Time series of evolution of activated fraction (N_d/N_a) under consideration of different approaches for the description of surface tension modification by organics. (a) 90% glutaric acid/10% ammonium sulphate; (b) 90% adipic acid/10% ammonium sulphate. Open squares, equation by *Facchini et al.* [1999]; solid circles, equation by *Langmuir* [1917] with constants derived from fitting of data by *Shulman et al.* [1996]; dashed line, no consideration of surface tension effects by organics; dot-dashed line, no consideration of surface tension effects by organics; composition: pure ammonium sulphate.

properties of an aerosol population [e.g., *Saxena and Hildemann*, 1996; *Brock et al.*, 2003]. We have investigated the modification of aerosol properties via aqueous production of organic aerosol mass (dicarboxylic acids $\leq C_6$) during cycling through clouds to show that on a mass-for-mass basis, the dicarboxylic acids formed in clouds exhibit cloud-nucleating behavior that is not significantly different from that of ammonium sulphate. In a first set of model runs we used processed aerosol compositions from our previous model study, characterized by high fractions of dicarboxylic acids mixed internally with ammonium sulphate, to show that drop number concen-

tration and drop effective radius are almost the same as for their pure ammonium sulphate counterparts. As discussed in part 1, the dicarboxylic acid fractions in these particles may be overestimated since they are relatively high compared to observations. Nevertheless, this appears to be of little consequence for the present study because the hygroscopic properties of the internally mixed particles are so similar to ammonium sulphate. The primary effect of aerosol modification by dicarboxylic acid formation ($\leq C_6$) via cloud cycling is through aqueous mass addition (sulphate and organic) rather than via composition differences. However, we cannot rule out, that additional chemical processes on or in cloud droplets might modify the properties (e.g., solubility, surface tension) of other organic compounds which contain more carbon atoms and/or functional groups. Nevertheless, at the current state of mechanism development of aqueous phase or heterogeneous surface chemistry models the impact of such processes on aerosol modification cannot be assessed.

[39] It has been shown that organic aerosol constituents (dicarboxylic acids $\leq C_6$) only have a significant influence on the N_d when solubility is low. In order to place an upper limit on the composition and solubility effects of the organics considered in our studies, we compared N_d resulting from pure ammonium sulphate aerosols and particles composed of 90% adipic acid and 10% ammonium sulphate. The adipic acid/ammonium sulphate particles show a marked delay in growth under all conditions applied here and lead to significant reductions in drop concentration. For example, at $w = 10 \text{ cm s}^{-1}$, the reduction in N_d is $\sim 50\%$. In general, it has been shown that these relative changes in N_d strongly depend on the location of the smallest activated size class relative to the mode of the aerosol size distribution.

[40] Finally, we have addressed the possible effects of surface tension changes by organics. Using a simplified approach for calculating the surface tension suppression by the species considered here, we have shown that the drop number reduction due to moderately soluble organics might be (partially) compensated for by the drop concentration increase due to surface tension suppression. Based on newly developed equations for the surface tension of aqueous solutions of individual dicarboxylic acids, we show that the empirical correlation between dissolved organics and surface tension suppression [*Facchini et al.*, 1999] might lead to an overestimate of the surface tension effects if only

Table 4. Comparison of N_d/N_a and r_e for Different Organic/Ammonium Sulphate Mixtures Applying Different Descriptions for the Surface Tension^a

	90% Adipic Acid/ 10% Ammonium Sulphate		90% Glutaric Acid/ 10% Ammonium Sulphate	
	$r_e, \mu\text{m}$	$N_d/N_a, \%$	$r_e, \mu\text{m}$	$N_d/N_a, \%$
(2)	8.6	80	8.3	90
(4)	8.2	95	8.0	100
Using coefficients for diacids based on fits to (3)	8.3	90	8.2	94

^aHere $r_g = 0.04 \mu\text{m}$, $\sigma = 2$, $w = 200 \text{ cm s}^{-1}$, 20 size classes.

dicarboxylic acids are considered. Confirmation of this result awaits further measurements of aerosol composition and its effects on surface tension.

[41] Yu [2000] and Mochida *et al.* [2003] point out the possible existence of organic salts with much lower solubilities (e.g., calcium oxalate) in aerosol particles. Thus, in our current model approach, we might have even overestimated the solubility of the organic acids (or their anions, respectively) so that under certain conditions the solubility of the organic fraction, i.e., in the form of salts, might be even lower.

[42] Although small dicarboxylic acids can represent a significant fraction of the soluble organic material in aged aerosols, the contributions of higher molecular weight organics to total aerosol organic carbon are not negligible. It is expected that the presence of high molecular weight organics in particles may affect particle solubility and surface tension. It is less likely that these species are formed in clouds, i.e., in dilute drops, since their longer chain, gas phase precursors are less soluble than those assumed for the small dicarboxylic acids. Thus including the chemical formation of such organics in aerosol/cloud models requires an extension of current chemical mechanisms. Besides heterogeneous processes on aerosol surfaces [Jang *et al.*, 2002], new particle formation is also a significant source for organic particulate matter [Hoffmann *et al.*, 1997; Kavouras and Stephanou, 2002].

[43] On the basis of the findings from our current study, we suggest that the description of mixed dicarboxylate/sulphate particles applied in modeling studies can be simplified for many conditions since their activation behavior does not differ significantly from pure ammonium sulphate particles. The conclusions of the present study can also be applied to other organic aerosol constituents exhibiting similar properties to dicarboxylic acids. The assessment of these modifications on cloud drop number concentrations awaits future studies.

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