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Joint effect of organic acids and inorganic salts on cloud droplet activation

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Joint effect of organic acids and inorganic salts on cloud droplet activation

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Received: 2 July 2010 – Accepted: 13 July 2010 – Published: 26 July 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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We have investigated CCN properties of internally mixed particles composed of one organic acid (oxalic acid, succinic acid, adipic acid, citric acid, cis-pinonic acid, or nordic reference fulvic acid) and one inorganic salt (sodium chloride or ammonium sulphate).

5 Surface tension and water activity of aqueous model solutions with concentrations relevant for CCN activation were measured using a tensiometer and osmometry, respectively. The measurements were used to calculate Köhler curves, which were compared to measured critical supersaturations of particles with the same chemical compositions, determined with a cloud condensation nucleus counter. Surfactant surface partitioning
10 was not accounted for. For the mixtures containing cis-pinonic acid or fulvic acid, a depression of surface tension was observed, but for the remaining mixtures the effect on surface tension was negligible at concentrations relevant for cloud droplet activation, and water activity was the more significant term in the Köhler equation. The surface tension depression of aqueous solutions containing both organic acid and inorganic salt was approximately the same as or smaller than that of aqueous solutions containing the same mass of the corresponding pure organic acids. Water activity was found to be highly dependent on the type and amount of inorganic salt. Sodium chloride was able to decrease water activity more than ammonium sulphate and both inorganic compounds had a higher effect on water activity than the studied organic acids, and
20 increasing the mass ratio of the inorganic compound led to a decrease in water activity. Water activity measurements were compared to results from the E-AIM model and values estimated from both constant and variable van't Hoff factors to evaluate the performance of these approaches. The correspondence between measurements and estimates was overall good, except for highly concentrated solutions. Critical supersaturations calculated with Köhler theory based on measured water activity and surface tension, but not accounting for surface partitioning, compared well with measurements, except for the solutions containing sodium chloride or one of the more surface active organic compounds. In such cases, significantly lower values were obtained from Köhler
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theory than the measured critical supersaturations, suggesting that surfactant partitioning and/or an effect of sodium chloride on solubility of the organic component is important.

1 Introduction

5 Atmospheric aerosols contain numerous organic and inorganic compounds. The organic fraction has been estimated to account for 20% to 90% of the total fine aerosol mass (Kanakidou et al., 2005). It has been shown that organic as well as mixed particles can influence cloud formation by acting as cloud condensation nuclei (CCN; e.g., Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Prenni et al., 2001; Giebl et al., 10 2002; Kumar et al., 2003; Bilde and Svenningsson, 2004; Broekhuizen et al., 2004; Rissman et al., 2007). The interactions between aerosols and water in the atmosphere leading to the formation of cloud droplets (the so-called indirect aerosol effect) can potentially have a great effect on the global radiation balance and global climate, but is not well understood (IPCC, 2007).

15 Köhler theory (Köhler, 1936) can be used to model cloud droplet formation and determine the critical supersaturation of aerosol particles if parameters such as surface tension and water activity of the aqueous solution droplet are available. However, for many atmospherically relevant species these parameters are not known. Furthermore, in internally mixed particles it is necessary to understand the interplay between the 20 different molecules and the effect of these interactions on water activity and surface tension.

Inorganic salts commonly found in the atmosphere (e.g. sodium chloride and ammonium sulphate) have only a small effect on the surface tension in aqueous solution (Low, 1969), and in activating aqueous solution droplets, surface tension can be approximated to the surface tension of pure water. This is not the case for many organic 25 components, such as humic-like substances (HULIS) or long-chained carboxylic acids, which can depress surface tension of aqueous solutions significantly (e.g., Shulman et

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al., 1996; Facchini et al., 1999; Kiss et al., 2005; Prisle et al., 2008). In the past few years some studies have been made on surface tension measurements of cloud water (Hitzenberger et al., 2002; Decesari et al., 2004), fog water and aerosol extract (Seidl and Hänel, 1983; Capel, 1990; Facchini et al., 2000; Decesari et al., 2004; Kiss et al., 2005), and also of individual organic compounds (Shulman et al., 1996; Ervens et al., 2004; Tuckerman and Cammenga, 2004; Varga et al., 2007). However, information about water activity of aerosol samples and model systems is still sparse, making it difficult to accurately predict critical supersaturation of particles composed of organic compounds or of mixtures of organic and inorganic compounds. So far, a few studies exist on cloud droplet formation of model mixtures, e.g., Gorbunov et al. (1999), Raymond and Pandis (2003), Henning et al. (2005), Svenningsson et al. (2006), Prisle et al. (2009), Kristensson et al. (2010).

When organic compounds are mixed with inorganic salts in aqueous solutions, two different effects on surface tension can be expected: either the surface tension of the solution is higher than in an aqueous solution of the pure organic component, because the salt has partially replaced the organic compound. Alternatively, the presence of inorganic salts in the solution can enhance the surface tension depression of organic surfactants by forcing the organic compound to the solution-air interface. Such a phenomenon was observed when cis-pinonic acid, fulvic acids or humic acids were dissolved in a 2 M ammonium sulphate aqueous solution (Shulman et al., 1996; Kiss et al., 2005).

In this study we focus on six organic and two inorganic compounds, which are considered atmospherically relevant (e.g., Saxena and Hildemann, 1996; Allen et al., 2000; Cheng et al., 2004): ammonium sulphate (AS), sodium chloride (SC), oxalic acid (OA), succinic acid (SA), adipic acid (AA), citric acid (CA) and cis-pinonic acid (cPA). In addition, we have studied the model substance nordic reference fulvic acid (NRFA) as a representative of HULIS. Water activity and surface tension have been determined experimentally for a series of aqueous solutions of mixtures of organic acids and inorganic salts and parameterized as a function of solute concentration. The parameteriza-

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tions are used in Köhler theory to calculate critical supersaturation as a function of the dry particle diameter, and the predictions are compared to experimentally determined critical supersaturations.

2 Theory

5 Köhler theory (Köhler, 1936) describes the saturation ratio, S , of water vapor over a solution droplet of a given radius, D_p :

$$S = \frac{p}{p_0} = a_w \cdot \exp\left(\frac{4M_w\sigma_{al}}{RT\rho D_p}\right) \quad (1)$$

where p is the water vapor pressure over the aqueous solution droplet, p_0 is the water vapor pressure over a flat water surface, a_w is the water activity in the droplet solution, σ_{al} is the air-liquid interfacial surface tension, M_w is the molar mass of water, R is the universal gas constant, ρ is the density of the droplet solution, and T is the absolute temperature (Seinfeld and Pandis, 1998).

The Köhler equation is the product of two effects: the Kelvin effect which describes how curvature increases the vapor pressure of water over an aqueous solution droplet; and the Raoult effect which depends on water activity and describes how the concentration of dissolved matter decreases the vapor pressure of water over an aqueous solution droplet. In this work, surface tension and water activity are parameterized as functions of weight percentage of the solutes in bulk aqueous solution. Limited solubility, as discussed by Bilde and Svenningsson (2004), and surfactant partitioning, as described by Li et al. (1998), Sorjamaa et al. (2004), and Prisle et al. (2008), are not accounted for in our calculations, but will be discussed in Sect. 4.3.

Water activity of a solution depends on the concentrations of the various chemical species dissolved in it. High density compounds with low molecular weights and high degrees of dissociation produce more species (molecules or ions) and thus efficiently

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reduce water activity. Without experimental data, water activity can be difficult to estimate, especially for complex mixtures where the various solutes may interact with solvent and with each other. We here calculate water activity in two ways and compare with experimental data: 1) with the state of the art thermodynamic aerosol model, E-AIM, (<http://www.aim.env.uea.ac.uk/aim/aim.php>, Clegg et al., 2001) or 2) by following the approach of e.g., Bilde and Svenningsson (2004) and calculating water activity from the van't Hoff factors of the individual compounds in solution:

$$a_w = \frac{n_w}{n_w + \sum_s i_s n_s}, \quad (2)$$

where n_w and n_s are the number of moles of water and solutes, respectively, and i_s is the van't Hoff factor of the solute s . The van't Hoff factor is defined as the ratio between the number of moles of species in aqueous solution and the number of moles of substance dissolved, and it is dependent on the concentration of solutes (e.g., Low, 1969). For a binary mixture with the mass ratio $X = m_1/m_2$ between the two compounds, Eq. (2) can be restated as:

$$a_w = \frac{n_w}{n_w + \sum_{s=1}^2 i_s n_s} = \frac{n_w}{n_w + i_1 n_1 + i_2 n_2} = \frac{n_w}{n_w + i_t n_t} \quad (3)$$

where n_t is the sum of n_1 and n_2 , the number of moles of the two compounds with molar masses M_1 and M_2 and van't Hoff factors i_1 and i_2 , respectively, and:

$$i_t = \frac{X \cdot i_1 \cdot M_2 + M_1 \cdot i_2}{X \cdot M_2 + M_1}. \quad (4)$$

For most non-electrolytes the van't Hoff factor is close to 1, but for strong acids or electrolytes the van't Hoff factor is typically larger. Van't Hoff factors for a series of inorganic compounds have previously been published (Low, 1969), and van't Hoff factors of monovalent acids in dilute aqueous solution can be estimated from the acid

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concentration c_s and the acid constant, K_a :

$$i_s = 1 + \frac{-K_a + \sqrt{K_a^2 + 4K_a \cdot c_s}}{2c_s} \quad (5)$$

This equation is also valid for polyvalent acids if the next dissociation steps are negligible compared to the first, i.e. if the first acid constant, K_{a1} is much smaller than the next acid constants, K_{a2} , K_{a3} , etc. (Frosch et al., 2010). For many atmospherically relevant compounds, information about water activity and van't Hoff factors is not available, and simplifications have been made by for example estimating the degree of dissociation in aqueous solution (Kiss and Hansson, 2004).

To describe solute concentration of aqueous solution droplets, we employ growth factors, GF, defined in the following way: when a particle with an initial dry diameter, d_0 , activates and takes up water, the diameter will increase to D_p . This growth can be expressed by the growth factor:

$$GF = D_p/d_0. \quad (6)$$

Because GF depends on the amounts of both water and solute, it is also an expression of solute concentration in an aqueous solution. For example, the growth factor is related to the weight percent (w/w%) of solute in solution by

$$GF = \left(1 + \frac{\rho_s}{\rho_w} \left(\frac{1}{0.01 \cdot w/w\%} - 1 \right) \right) \quad (7)$$

where ρ_s and ρ_w are the densities of the dry particle and of water, respectively, and weight percent is with respect to weight of the solution including water (solvent) and all solutes.

In case of solutions containing one organic acid and one inorganic salt the weight percent is defined as:

$$w/w\% = \frac{m_o + m_i}{m_o + m_i + m_w}, \quad (8)$$

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where m_w , m_i and m_o are the masses of water, the inorganic and the organic component, respectively. The growth factor is determined according to Eq. (7), using a density, ρ_s , calculated as

$$\frac{1}{\rho_s} = \frac{X_{\text{organic}}}{\rho_{\text{organic}}} + \frac{1 - X_{\text{organic}}}{\rho_{\text{inorganic}}} \quad (9)$$

5 where ρ_{organic} and $\rho_{\text{inorganic}}$ are the densities of the organic and inorganic compound, respectively, and X_{organic} is the mass fraction of the organic compound in the initial dry particle.

3 Experimental

10 In this study, nine different mixtures between organic acids and the inorganic salts sodium chloride and ammonium sulphate were investigated, see Table 1. Most chemicals for surface tension, osmolality, and CCN measurements were obtained from commercial sources: ammonium sulphate (Sigma-Aldrich, 99.999%), sodium chloride (Riedel-deHaën, 99.8%), adipic acid (Aldrich, 99%), citric acid (Aldrich, >99.5%), oxalic acid (Fluka, >99.5%), succinic acid (Fluka, 99.5%), cis-pinonic acid (Aldrich, 98%) and used as received. NRFA was purchased from the International Humic Substance Society (<http://www.ihss.gatech.edu/index.html>). Aqueous solutions were prepared by dissolving chemicals in double-deionized water purified using a MilliQ Plus Ultrapure water system.

15 Measurements of osmolality and surface tension were performed at University of Pannonia. First, solutions of mixtures with growth factors of relevance to cloud droplet activation (GF=2–12) were prepared. Osmolality and surface tension measurements were carried out when both the organic and inorganic components were entirely dissolved. Osmolality was measured with a KNAUER K-7400 Semimicro osmometer. This method considers all of the processes in the solution (e.g. dissociation of solute, interaction between solute and solvent). For one measurement, 0.15 ml solution was

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used. The measurement time was approximately 2 min; the measuring range was 0–2000 mOsm kg⁻¹. Water activity was calculated from the measured osmolality, as described by Kiss and Hansson (2004). Surface tension of the solutions was measured with an FTÅ 125 tensiometer, which uses pendant drop shape analysis. From one drop of solution, 40 parallel measurements were performed during 10 s at room temperature. The volume of the droplet was approximately 10 µl corresponding to a curvature radius of 1.3 mm.

Critical supersaturations of the mixtures were determined experimentally at the University of Copenhagen. The experimental setup has been described previously (Bilde and Svenningsson 2004; Svenningsson et al., 2006), and is briefly presented here: aerosol particles were produced from a bulk aqueous solution of the desired chemical composition using a constant output atomizer (TSI, 3076). During aerosol production, the aqueous solution was continuously stirred to ensure a homogeneous distribution of solutes in solution, i.e. prevent the surface active compounds from concentrating in the solution surface. The produced particles are assumed to be internally mixed and have the same chemical composition as in the aqueous solution. The particles were dried in diffusion driers using silica gel and mixed with dried, particle free air. The relative humidity of the aerosol flow was measured several times during the experiments and was always found to be below 12%. A specific particle diameter was selected using a differential mobility analyzer (DMA, TSI 3080) before the aerosol flow was divided between a condensation particle counter (CPC, TSI 3010) and a static thermal diffusion cloud condensation nucleus counter (CCNC, University of Wyoming CCNC-100B). The CPC measured the total concentration of particles, whereas the CCNC detected the number of activated particles at a specified supersaturation (SS) of water. The supersaturation in the CCNC could be varied stepwise between 0.2 and 2.0%. The critical supersaturation (SSc) was determined using the relaxed step transfer function (Svenningsson and Bilde, 2008) assuming full solubility. The CCNC was calibrated using ammonium sulphate as described by for example Bilde and Svenningsson (2004). Points for the calibration line were obtained both before, during and after the actual experiments were

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performed. The same calibration was used for all experiments.

4 Results and discussion

4.1 Surface tension

Surface tension was measured in model solutions of the six 50:50 organic-inorganic mixtures containing ammonium sulphate (measurements at selected weight percentages are shown in Table 2; the full data sets are shown in Fig. 1). For each mixture, best fits were obtained from a wide variety of functions. These are given in Table 3 together with the appropriate concentration range of validity, i.e. the concentration range of the surface tension measurements. Figure 1 shows the measured surface tensions as a function of growth factor (i.e. the total solute concentration in aqueous solution).

The mixtures can be separated into three different groups: for the mixtures containing oxalic acid, no deviation is seen from the surface tension of pure water. For mixtures containing succinic acid, adipic acid, or citric acid, a slight surface tension depression is observed in the concentration range relevant for activation. And for the remaining two series of mixtures, ammonium sulphate mixed with NRFA and with cis-pinonic acid, respectively, surface tension is significantly lowered. This is a consequence of the fact that both fulvic acid and cis-pinonic acid are effective surfactants (Shulman et al., 1996; Kiss et al., 2005; Varga et al., 2007). The surface tension of pure cis-pinonic acid in aqueous solution is also shown for comparison in Fig. 1. At a given growth factor, the surface tension is lower in a solution of the pure cis-pinonic acid than in a solution containing a mixture between cis-pinonic acid and ammonium sulphate. Neglecting the effects of surfactant partitioning, this means that for example at $GF = 6$ the surface tension of a pure cis-pinonic acid droplet solution is $59 \pm 0.6 \text{ mN m}^{-1}$ (Varga et al., 2007) whereas it is $62 \pm 0.6 \text{ mN m}^{-1}$ for a droplet solution of the same size formed on a mixed particle. This difference in surface tension is caused by ammonium sulphate replacing cis-pinonic acid, leading to a lower concentration of the surfactant.

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If, instead, the surface tension is depicted as a function of the concentration of organic matter, a slightly different picture arises (see Fig. 2): now, the same amount of organic surfactant has a similar effect on surface tension in the ternary solution with salt as in the binary solution of cis-pinonic acid and water. Note, that the mass ratio between the organic acid and ammonium sulphate is 50:50. Therefore, when the weight percentage of the organic in aqueous solution increases, the inorganic weight percentage also increases for all mixtures. This means that if a salting-out effect on surface tension, similar to that reported by e.g., Shulman et al. (1996) and Kiss et al. (2005), could be observed, it should be even more pronounced in high weight percentage solutions. For the solutions containing succinic acid, adipic acid, or citric acid, Fig. 2b–d shows that, similarly to the mixtures containing cis-pinonic acid, the surface tension depression as a function of the organic concentration is not changed notably when ammonium sulphate is present. The deviation between this result and observations reported earlier (Shulman et al., 1996; Kiss et al., 2005) can be explained by the difference in the concentration of inorganic salt. Shulman et al. (1996) as well as Kiss et al. (2005) used 2 M ammonium sulphate to study the enhancement of surface tension depression of organic surfactants. Ammonium sulphate in that concentration can be present in the very early phase of droplet formation (i.e. $GF < 2$). However, in our experiments, the concentration of ammonium sulphate was significantly lower (< 0.1 M), which is relevant for the conditions around activation. As a consequence, the salting-out effect of ammonium sulphate was not observed, the only exception being citric acid for which a solution with $GF = 2$ (corresponding to a weight percentage of 10%) was studied. This solution had a higher surface tension than the corresponding solution containing both citric acid and ammonium sulphate (see Fig. 2d).

To the best of our knowledge, the surface tension as a function of concentration of pure NRFA in aqueous solution has not been reported in the literature. Therefore, it is not possible to evaluate the effect of ammonium sulphate on the surface tension in aqueous solutions containing NRFA.

We conclude that, under the conditions relevant for cloud droplet activation of aerosol

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particles, the surface tension depression of droplet solutions formed on 50:50 mixed particles containing surfactants is approximately equal to or slightly lower than that of droplet solutions formed on particles of the same size composed of the corresponding pure organic compound. Note that a lower surface tension depression corresponds to a higher surface tension. Significant enhancement of surface tension depression in the presence of salt compared to pure organic compounds is not observed even when surface tension is depicted as a function of the concentration of the organic compound, i.e. we do not detect any salting-out effect in the concentration range relevant for cloud droplet activation. In the solutions containing oxalic acid, adipic acid, succinic acid, and citric acid the surface tension depression at concentrations relevant for activation was small, and it can be concluded that for these mixtures, water activity will be the main factor determining critical supersaturation.

4.2 Water activity

Water activity was determined as a function of growth factor in solutions containing organic acids and ammonium sulphate, see Fig. 3. A best fit was determined for water activity data at each concentration level, see Table 3. Data at selected weight percentages are tabulated in Table 4; for the full data sets, see Fig. 3.

First, mixtures with a 50:50 mass ratio between ammonium sulphate and organic acids will be discussed: high density compounds with low molecular weight and high van't Hoff factor produce more species (ions and molecules) at any given growth factor and most efficiently reduce water activity. Ammonium sulphate is a stronger electrolyte than most of the organic acids studied and consequently produces the most ions at a given growth factor, see Table 5. The only exception is oxalic acid, which is a relatively strong electrolyte and has higher density and lower molecular weight than ammonium sulphate. At a given growth factor, oxalic acid produces a similar number of molecular species per volume unit of dry material ($2.8 \times 10^4 \text{ mol/m}^3$ at $\text{GF}=4$, see Table 5 for details) as ammonium sulphate ($2.9 \times 10^4 \text{ mol/m}^3$ at $\text{GF}=4$, see Table 5). Therefore, oxalic acid is expected to lower water activity to the same extent as ammo-

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5 nium sulphate. This line of thinking is confirmed by Fig. 4a, which shows that mixtures
of oxalic acid and ammonium sulphate have similar effect on water activity as pure am-
monium sulphate. It is reasonable to approximate the surface tension of solutions of
mixtures of oxalic acid and ammonium sulphate, and solutions containing either pure
10 ammonium sulphate or pure oxalic acid with the surface tension of pure water. This
approximation is based on the facts that ammonium sulphate as well as oxalic acid
has negligible effect on the surface tension in dilute solutions (Low, 1969; Varga et al.,
2007), and that the 50:50 mixture of ammonium sulphate and oxalic acid has a neg-
ligible effect on surface tension at activation conditions, as concluded in Sect. 4.1.
15 Therefore, particles composed of a mixture of oxalic acid and ammonium sulphate will
have a similar Kelvin term as particles composed of either pure oxalic acid or pure am-
monium sulphate. Consequently, both particles composed of mixtures of oxalic acid
and ammonium sulphate and pure oxalic acid particles are expected to activate simi-
larly to pure ammonium sulphate particles. This hypothesis will be further elaborated
in Sect. 4.3.

Next, we proceed to another series of experiments also displayed in Fig. 4, in which
the effects of the ratio of the organic acid to inorganic salt and the importance of the
type of inorganic salt (ammonium sulphate versus sodium chloride) on water activity
were studied. Four types of mixtures were prepared: oxalic acid mixed with either am-
monium sulphate or sodium chloride with a mass ratio of either 50:50 or 80:20. Water
20 activities of these solutions are shown in Fig. 4a and b. As discussed above, ammo-
nium sulphate produces similar amounts of ions as oxalic acid at a given growth factor.
This is seen in Fig. 4a, where the measured water activities of 50:50 mixtures of oxalic
acid and ammonium sulphate are quite similar to the 80:20 mixtures of oxalic acid
and ammonium sulphate. Both sets of measurements are also close to the water activities
25 of pure ammonium sulphate solutions, reported by Low (1969). This is not the case for
the mixtures of sodium chloride and oxalic acid. The higher density and lower molec-
ular weight of sodium chloride result in a higher concentration of dissociated sodium
chloride entities at a concentration corresponding to $GF=4$ (see Table 5) and a lower

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water activity at a given growth factor in aqueous solutions of pure sodium chloride than in mixtures of oxalic acid and ammonium sulphate. Consequently, a higher mass fraction of sodium chloride in aerosol particles containing oxalic acid – or a compound with similar physical and chemical properties – corresponds to lower water activity and thereby also a greater ability to act as CCN at a given supersaturation. Furthermore, sodium chloride has a greater effect on water activity than ammonium sulphate. This can be seen from Fig. 4b, where water activity of the mixtures containing sodium chloride is lower than the water activity of the two mixtures containing ammonium sulphate for all growth factors. This is most clearly seen by a comparison with the curve showing the modeled water activity of pure oxalic acid (dotted black line) which is shown in both Fig. 4a and b. The mixture with the highest content of sodium chloride (the 50:50 mixture, light blue squares) lowers water activity the most.

The effect of the type and amount of the inorganic component on water activity is also significant for mixtures containing organic compounds which produce less species in aqueous solutions than oxalic acid (e.g. weaker acids or compounds with low water solubility, lower density or higher molar mass). This can be seen in Fig. 5a by comparing the water activity for pure citric acid to the 50:50 mixtures of citric acid and ammonium sulphate. The water activity of a solution containing only citric acid is higher than the water activity of solution composed of a 50:50 mixture with ammonium sulphate for all concentrations. As seen from Table 5, at a given growth factor, all organic compounds (except oxalic acid) dissociate into a significantly lower number of molecules than ammonium sulphate. Therefore, when the mass ratio of ammonium sulphate increases, for example from 0 to 50%, the number of dissociated molecular species increases, and the water activity decreases. This is also the case for the remaining organic acids investigated in this study, as can be seen from Fig. 5b–d. This can have a great effect on CCN activity since the saturation ratio is directly proportional to the water activity, see Eq. (1). For example, Fig. 4 and the parameterization in Table 3 shows that at $GF=4$, $a_w=0.995$ for the 50:50 mixture between citric acid and ammonium sulphate. Varga et al. (2007) reports that at the same growth factor, $a_w=0.997$ for pure citric acid.

Using Eq. (1) (assuming the surface tension to equal that of pure water), it can be calculated that a critical concentration of $GF=4$ corresponds to a critical saturation ratio of 1.011 for the 50:50 mixture and 1.013 for pure citric acid. Thus, a 0.2% difference in water activity will lead to a $\sim 20\%$ difference in supersaturation (from 1.1% to 1.3%).

Figures 4 and 5 illustrate that the type and relative quantity of the inorganic component has a significant effect on the water activity of an aqueous solution droplet and thereby on activation. In Fig. 5, the measured water activities are also compared to predictions from the E-AIM model and from calculations using estimated van't Hoff factors, see Eq. (3). The van't Hoff factors were determined according to Eq. (4) in two different ways; either calculated as a function of the concentration of the individual species (using Eq. (5) and literature data reported by Low (1969) and Young and Warren (1992)), or by assuming that the inorganic salt is fully dissociated and that the organic is not dissociated, independently of the solute concentration (similar to the approaches of e.g., Cruz and Pandis, 1997; Bilde and Svenningsson, 2004; Kristensson et al., 2010). Water activity calculated in this way, using either variable or constant van't Hoff factors, yields a good agreement with measured data, but the E-AIM results gives an even better agreement. This confirms the ability of the E-AIM model to accurately calculate water activity for atmospherically relevant aqueous solutions. In the more concentrated solutions, however, the model seems to slightly underpredict the measured water activity.

Of the four mixtures displayed in Fig. 5, the greatest deviations between calculated and measured water activity is observed for mixtures containing citric acid. These results are further emphasized in Fig. 6 which, for comparison, also displays data for the 50:50 mixtures between oxalic acid and either ammonium sulphate or sodium chloride. Figure 6 compares calculated or modeled water activity, $a_w(\text{calc})$, with measured water activities, $a_w(\text{meas})$. The measured water activity is also displayed in Fig. 3, and $a_w(\text{calc})$ is water activity determined either with the E-AIM or from van't Hoff factors estimated as described above. The ratio between $a_w(\text{calc})$ and $a_w(\text{meas})$ is displayed as a function of growth factor. For high growth factors (dilute solutions) the methods

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for calculating a_w compare well with measurements (i.e. the ratio is approximately 1). For lower growth factors deviations are observed. The consequences of these deviations are explored further in Fig. 7, where two examples of Köhler curves are displayed calculated as in Eq. (1). The water activity is based on either measurements, results from E-AIM or from estimated van't Hoff factors for two dry particle diameters, $d_0=30$ and 100 nm. For simplicity, the red curves in Fig. 7 are calculated using constant van't Hoff factors. Figure 7a shows that for $d_0=30$ nm, the critical supersaturation is 0.919% using measured water activity, 1.14% using E-AIM results and 1.11% using estimated van't Hoff factors. In Fig. 7b, $d_0=100$ nm and the critical supersaturation is 0.150% using measured water activity, 0.166% using E-AIM results and 0.179% using estimated van't Hoff factors.

From this example it is seen that the deviation in predicted critical supersaturation related to using calculated water activity instead of a parameterization of measurements is larger for smaller dry particle diameters (corresponding to more concentrated solution droplets), and less significant for larger dry particle diameters (corresponding to less concentrated solution droplets).

4.3 Critical supersaturations

When the Raoult and Kelvin effects are known, Köhler curves can be calculated according to Eq. (1) for a particle of a given dry size. Critical supersaturations have thus been determined for mixed particles with a dry size between 25 nm and 125 nm, using $T=298.15$ K and $\rho=\rho_w$, i.e. the aqueous solution density is equated to the density of pure water at room temperature. These results are depicted in Figs. 8–10. The lines in the figures represent the calculated results based on surface tension and osmolality measurements (parameterizations shown in Table 3) while the individual data points (listed in Table 6) are measured values of the critical supersaturation. For the smallest particle diameters surface tension and water activity parameterizations have been extrapolated outside the validity ranges given in Table 3. In Figs. 8–10, the extrapolated sections are indicated by dashed lines.

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Figure 8 shows activation of the oxalic acid mixtures. Since neither oxalic acid nor the inorganic salts affect surface tension of the droplet solution significantly, water activity in the aqueous solution droplets should be the factor determining critical supersaturation. Consequently, Köhler theory predicts that particles composed of mixtures of oxalic acid and inorganic salt with mass ratio 50:50, i.e. with the highest content of inorganic salt, (light blue and green lines) should activate most easily, because water activity depression for these mixtures are highest. The two series of mixtures of oxalic acid and inorganic salt with mass ratios 80:20 (red and dark blue lines) activate at a higher supersaturation. Measured critical supersaturations of the two series of mixtures containing oxalic acid and ammonium sulphate are slightly underpredicted by Köhler theory, but the CCNC results of mixed particles of oxalic acid and sodium chloride in the mass ratio 80:20 deviate significantly from Köhler theory. These deviations will be discussed below.

The mixed particles containing either one of the three other organic weak surfactants (citric acid, adipic acid, and succinic acid, respectively) and ammonium sulphate activate at higher supersaturations than the mixtures with oxalic acid (see Fig. 9) because these organic compounds have a weaker effect on water activity than oxalic acid. None of these acids have a strong effect on surface tension at activation and thus water activity is expected to be the dominant factor in determining the critical supersaturation.

For the mixtures containing citric acid and ammonium sulphate (black symbols), in most cases the deviations between measured data and the Köhler curve are within experimental error, whereas the difference between modeled and measured critical supersaturations for particles composed of succinic acid and ammonium sulphate (blue symbols) is somewhat larger and it is considerable for particles composed of adipic acid and ammonium sulphate (red symbols). For these particles, using the surface tension of pure water in the Kelvin term of the Köhler equation results in better agreement with experimental data (red dotted line). In the calculated Köhler curves surface tension depression is accounted for but the effects of partitioning are neglected. The possible effect of surfactant partitioning will be discussed below.

In contrast to the organic acids discussed above, both NRFA and cis-pinonic acid have a strong effect on surface tension. In Fig. 10, Köhler theory predicts that these mixtures should activate almost as easily as the mixtures containing oxalic acid. The low critical supersaturation is related to the strong depression of surface tension. Mixed particles containing cis-pinonic acid and ammonium sulphate proved difficult to study experimentally, and critical supersaturations for these mixed particles are not reported, but measurements show that particles containing NRFA activate at a supersaturation much higher than predicted by Köhler theory using a parameterization of surface tension based on measurements, but neglecting partitioning. For comparison, a Köhler curve is re-calculated using the surface tension of water which gives a much better agreement with measured critical supersaturation. This is also in concordance with the conclusions of Prisle et al. (2008).

There are several ways to account for deviations between measured and modeled critical supersaturation. One possible explanation is that particles partially evaporated before entering the CCNC, but after size selection in the DMA. In that case, the particles would activate with more difficulty because of their smaller size, and the measured critical supersaturations would be overestimated. Such an effect has been observed for example for glutaric acid particles (Frosch et al., 2010). However, all experiments were performed at room temperature, and the residence time in the tubing and instruments between size selection and activation was approximately 1–2 s. None of the investigated organic compounds are known to be volatile at room temperature, (e.g., Yaws, 1994; Bilde and Pandis, 2001; Bilde et al., 2003) and no sign of significant evaporation was observed during experiments.

It is also possible that activation and droplet growth were limited because of low solubility of the components of the aerosol particles. Although all of the investigated compounds are fairly water soluble, it is well known that the presence of inorganic salts can diminish the solubility of organic compounds (e.g., Streng, 2001; Hefter and Tomkins, 2003). If the particle is not fully soluble, a core of solid material will remain at activation and less solute will be in the aqueous solution droplet (Bilde and Sven-

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ningsson, 2004). This will influence both the water activity and surface tension, and it can lead to an underestimation of the modeled critical supersaturation. In the model solutions used for determining surface tension and water activity, no precipitate was observed for $GF > 4$, indicating that the mixtures were fully soluble at activation conditions, but the model solutions might have been supersaturated. The exact effect of sodium chloride and ammonium sulphate on the solubility of the investigated organic acids should be investigated further, in particular the effect of sodium chloride on the solubility of oxalic acid.

Mass transfer limitation on the growth of activating droplets can also decrease the number concentration of droplets formed, even above the critical supersaturation (Nenes et al., 2001; Ruehl et al., 2008). It has been suggested that for example the formation of surface films can delay droplet growth (Asa-Awuku et al., 2009). Such effects could lead to fewer activated particles being detected in the CCNC and an overestimation of the supersaturation necessary to activate the studied particles. However, it was not possible to evaluate growth kinetics for these data sets.

Finally, the deviations between measured and modeled critical supersaturation may be related to surfactant partitioning, which can lead to an enhancement of water activity and surface tension. Droplets on the nano- or micrometer scale have much larger surface-to-volume ratios than macroscopic bulk solutions. Since surface active compounds are preferentially located at the surface, this means that a larger fraction of the surface active molecules can be present close to the surface of a droplet, relative to a macroscopic solution with the same concentration of surfactant. If a relatively large amount of surfactant molecules is residing in the surface of a droplet, the droplet bulk will be depleted, causing the surfactant to have a smaller effect on water activity (Sorjamaa et al., 2004; Prisle et al., 2008, 2010). At the same time, this will affect the Kelvin term (Li et al., 1998; Sorjamaa et al., 2004; Prisle et al., 2008) since the depression of the Kelvin term will be smaller than if partitioning was not accounted for. Neglecting surfactant partitioning may lead to a significant underestimation of the critical supersaturation (Li et al., 1998; Sorjamaa et al., 2004; Prisle et al., 2008, 2010). This effect

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seems to be in play for the particles containing the more surface active compounds studied; in particular NRFA. Although we were not able to confirm it experimentally, surfactant partitioning is also expected to be important for particles containing cis-pinonic acid (Sorjamaa et al., 2004).

5 Conclusions

The CCN ability of particles composed of different organic acid-inorganic salt mixtures was investigated by measuring the surface tension and water activity of droplet solutions and comparing Köhler theory to measured critical supersaturations.

The surface tension depression was in most cases negligible in the concentration range relevant at activation and only the very early phase of droplet growth, where the solute concentration is high, would be influenced by the surface tension effect of these compounds. Since activation occurs in very dilute aqueous solutions droplets, there should be no effect on the critical supersaturation. This, however, does not apply to the mixtures containing NRFA or cis-pinonic acid. Solutions containing one of these organic surfactants and ammonium sulphate showed a significant surface tension depression at activation conditions, but compared to aqueous solutions of the pure cis-pinonic acid as reported by Varga et al. (2007), the effect of organic-inorganic mixtures on surface tension was smaller when seen as a function of growth factor. The presence of inorganic salts can therefore influence activation behavior by decreasing surface tension depression.

Water activities of the solutions were mainly influenced by the presence of inorganic salts due to the higher degree of dissociation. At a given growth factor, the water activity of an organic acid-inorganic salt mixture was higher than for the pure inorganic salt but lower than for the pure organic compound. Consequently, the chemical species and mass fraction of the inorganic salt can significantly influence activation: particles with higher inorganic content were found to activate at lower critical supersaturation. The only exception was the mixtures containing oxalic acid and ammonium sulphate. The

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activation behavior of such mixed particles depended only slightly on the mass ratio between the organic and inorganic compounds. A good correspondence was observed between measured water activity and the E-AIM model, confirming the atmospheric relevance of this thermodynamic model. A good correspondence was also observed between measured water activities and water activities calculated from estimated van't Hoff factors. However, in both cases significant deviations between measurements and models at activation of particles with small dry diameters were observed.

For mixed particles containing ammonium sulphate as the salt, Köhler theory based on parameterizations of surface tension and water activity compares well with experimentally obtained values of the critical supersaturation, except for particles containing the more surface active compounds, in particular NRFA. In these cases the critical supersaturation is significantly underpredicted and better described using the surface tension of water. This is ascribed to effects of surfactant partitioning.

Köhler theory based on parameterizations of surface tension and water activity underpredicts observed critical supersaturations for mixed particles of oxalic acid and sodium chloride suggesting that the influence of sodium chloride on the solubility of the organic acid should be investigated further.

Acknowledgements. We acknowledge the FP6 projects Atmospheric Composition Change: an European network (ACCENT, contract No: GOCE-CT-2004-505337) and European Integrated project on Aerosol Cloud Climate and Air Quality interactions (EUCAARI, contract No: 036833-2) The authors would also like to thank the Hungarian Academy of Sciences for financial support and Hans-Christen Hansson at Stockholm University for lending the FTA 125 tensiometer for the measurements.

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Table 1. List of mixtures containing oxalic acid (OA), ammonium sulphate (AS), sodium chloride (SC), succinic acid (SA), citric acid (CA), cis-pinonic acid (cPA), adipic acid (AA) and Nordic reference fulvic acid (NRFA).

Mixture	Mass fraction
OA+AS	50:50
OA+AS	80:20
OA+SC	50:50
OA+SC	80:20
SA+AS	50:50
CA+ AS	50:50
cPA+ AS	50:50
AA+AS	50:50
NRFA+AS	50:50

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Table 2. Surface tension (σ) as a function of weight percentage (w/w%) for the 50:50 mixtures between an organic acid and ammonium sulphate (AS).

w/w%	σ /mN/m					
	Oxalic acid+AS, 50:50	Succinic acid+AS, 50:50	Adipic acid+AS, 50:50	Citric acid+AS, 50:50	NRFA +AS, 50:50	Cis-pinonic acid+AS, 50:50
0.1	72	72	72	72	70	69
0.5	72	72	71	72	63	62
1	72	71	69	72	61	59
2	–	71	–	72	–	56
5	72	69	–	71	–	–
10	–	–	–	70	–	–
20	–	66	–	66	–	–

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Table 3. Fitted functions of surface tension and water activity as a function of growth factor (x =GF) for the studied 50:50 mixtures containing ammonium sulphate.

	Surface tension, σ / mN/m	Water activity, a_w	Range, x
OA+AS	$\sigma = \sigma_w$	$0.9997 \cdot \exp(-\exp(-2.589 - 0.5595 \cdot x))$	4–13
SA+AS	$72.3 \cdot \exp(-\exp(-0.850 - 0.759 \cdot x))$	$(2.139 + x^{2.802}) / (2.464 + x^{2.802})$	5–11
AA+AS	$72.6 - 403 \cdot \exp(-1.928 \cdot x^{0.542})$	$0.9996 \cdot \exp(-\exp(-2.805 - 0.634 \cdot x))$	2–12
CA+AS	$72.0 / (1 + 9.916 \cdot \exp(-2.320 \cdot x))$	$(0.870 + x^{3.305}) / (1.358 + x^{3.305})$	2–12
NRFA+AS	$70.2 / (1 + \exp((22.8 - 2.233 \cdot x)^{0.0159}))$	$0.9998 \cdot \exp(-\exp(-3.20 - 0.580 \cdot x))$	6–12
cPA+AS	$69.9 - 18.4 \cdot \exp(-0.00111 - x^{2.406})$	$(2.911 + x^{2.714}) / (3.073 + x^{2.714})$	3–11

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Table 4. Water activity (a_w) as a function of growth factor (w/w%) for the 50:50 mixtures between an organic acid and ammonium sulphate.

w/w%	Oxalic acid+AS	Succinic acid+AS	Adipic acid+AS	Citric acid+AS	NRFA +AS	Cis-pinonic acid+AS
0.1	0.9997	0.9996	0.9997	0.9997	0.9998	0.9997
0.5	0.9986	0.9991	0.9989	0.9988	0.9992	0.9988
1	0.9971	0.9967	0.9976	0.9975	0.9985	0.9980
2	0.9949	0.9939	–	0.9956	–	0.9965
5	–	0.9846	–	0.9879	–	–
20	–	–	–	0.9571	–	–

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Table 5. Physical properties of the studied compounds.

Compounds	Molar mass (kg/mol)	Density (kg/m ³)	pK _{a1}	Van't Hoff factor ^b , GF=4	Entities per volume dry aerosol, GF=4 ^c (mol/m ³)
Sodium chloride	0.05844	2164	–	1.8639	69212
Ammonium sulphate	0.13214	1769	–	2.1903	29322
Oxalic acid	0.09004	1900	1.25	1.3364	28201
Succinic acid	0.11809	1572	4.21	1.0171	13539
Adipic acid	0.14614	1362	4.42	1.0160	9469
Citric acid	0.19212	1665	3.13	1.0713	9284
Cis-Pinonic acid	0.18423	786	~7	1.0012	4271
NRFA ^a	2.18	~1500	~7	~1	~700

^a Molar mass of NRFA from Persson et al., the density and acidity constants of NRFA are arbitrary estimates.

^b The van't Hoff factor of the organic acids has been determined from Eq. (5) using the first acid constant. The van't Hoff factor of the inorganic salts have been estimated from the data of Low (1969) and Young and Warren (1992).

^c Determined as $i_s \cdot n_s / V_p$ where i_s is the van't Hoff factor of compound s in an aqueous solution with GF=4, n_s is the number of moles of s in a particle with the volume unit volume, $V_p = 1 \text{ m}^3$.

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Table 6. Critical supersaturation as a function of dry particle diameter for the studied mixtures.

OA+AS 50:50		OA+AS 80:20		OA+SC 50:50		OA+SC 80:20	
d_0/nm	SS/%	d_0/nm	SS/%	d_0/nm	SS/%	d_0/nm	SS/%
31	1.0776	35	0.8509	30	0.9634	45	1.1091
33	0.9639	40	0.6900	31	0.9040	47	0.7563
35	0.8530	42	0.6690	33	0.8236	50	0.5799
38	0.7601	44	0.6112	35	0.7577	52	0.5642
40	0.7013	45	0.5610	37	0.6520	60	0.4027
45	0.6137	46	0.5984	40	0.6028	65	0.3658
50	0.4975	48	0.5422	42	0.5648	70	0.3220
55	0.4250	50	0.5122	45	0.5449	75	0.2839
60	0.3677	60	0.4041	50	0.4481	80	0.2689
65	0.3504	70	0.3082	55	0.4032	85	0.2341
70	0.3005	80	0.2403	60	0.3566	90	0.2266
75	0.2919	90	0.2260	65	0.3018	95	0.1955
80	0.2498			70	0.2961	100	0.2172
90	0.2228			80	0.2343		
95	0.2231			88	0.1960		
				95	0.1509		

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Table 6. Continued.

AA+AS		CA+AS		NRFA+AS		SA+AS	
d_0/nm	SS/%	d_0/nm	SS/%	d_0/nm	SS/%	d_0/nm	SS/%
33	1.0621	35	1.0141	35	1.1179	30	1.1492
35	1.0425	37	0.9158	38	0.9967	31	1.0740
37	0.9753	38	0.9404	38	1.0260	33	0.9914
38	0.9192	40	0.9431	40	1.0371	35	0.8848
40	0.8138	42	0.7703	42	0.8523	37	0.8744
45	0.7562	47	0.6612	42	1.0195	39	0.7606
47	0.6986	52	0.5558	45	0.7874	41	0.7254
50	0.653	57	0.4869	45	0.8989	44	0.6374
52	0.5435	55	0.5503	47	0.737	47	0.5747
55	0.6035	60	0.4439	50	0.7394	50	0.5312
57	0.4800	62	0.4214	52	0.6187	55	0.4409
60	0.4451	65	0.4191	55	0.5778	60	0.3822
60	0.4941	67	0.3723	60	0.5412	65	0.3444
65	0.4421	75	0.3354	65	0.4577	70	0.3293
70	0.3740	85	0.2899	70	0.4428	75	0.2978
75	0.3191	95	0.2248	75	0.3589	80	0.2581
80	0.2964	100	0.2123	80	0.3577	85	0.2312
85	0.2573			85	0.3020	90	0.2249
90	0.2472			90	0.3200	95	0.2027
95	0.2421			95	0.2703	100	0.2021
100	0.2121						

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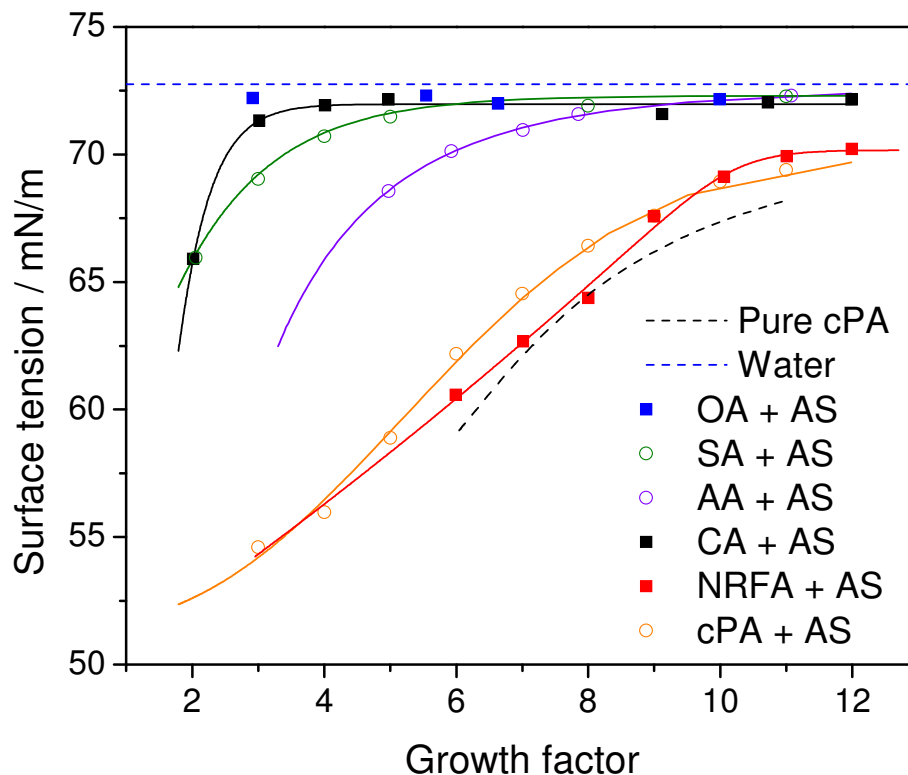


Fig. 1. Measured surface tension of the 50:50 mixtures containing an organic acid and ammonium sulphate. Continuous lines based on empirical fits (see Table 3) are included to aid visual inspection. A parameterization of the surface tension of pure cis-pinonic acid in aqueous solution (Varga et al., 2007) is included for comparison.

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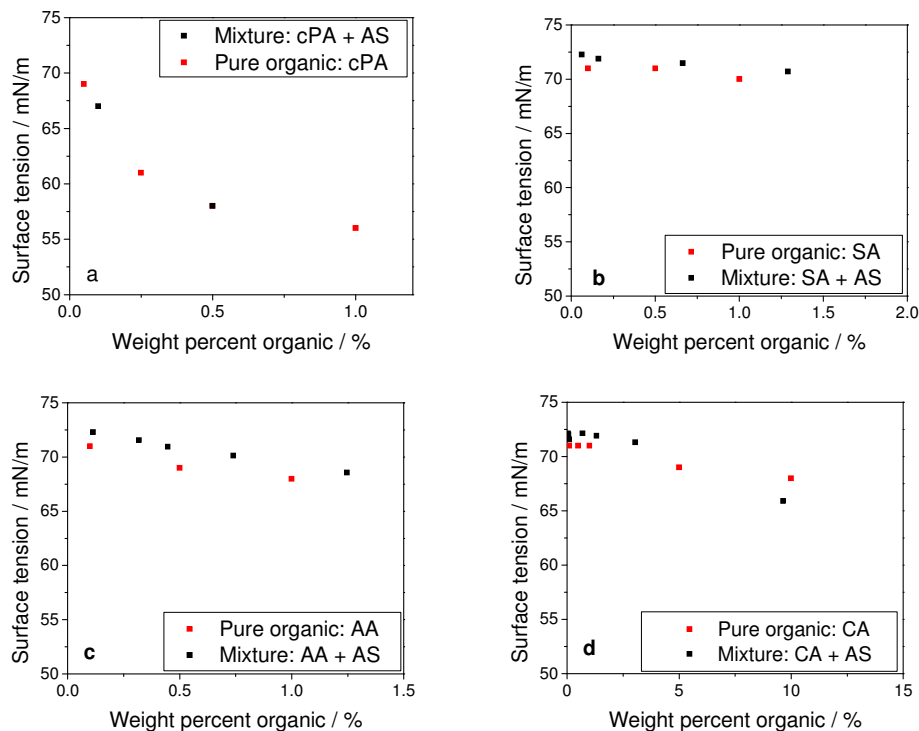


Fig. 2. Measured surface tension for four of the studied 50:50 mixtures. The data is depicted as a function of weight percentage of the organic compound. The data for pure organic acids is obtained from Varga et al. (2007).

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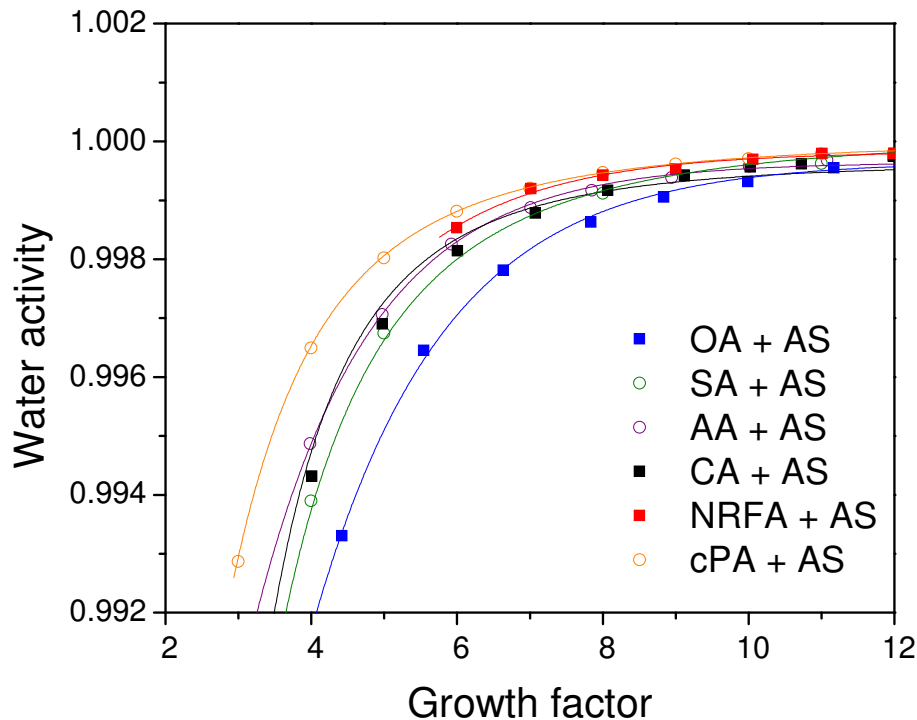


Fig. 3. Measured water activity of the 50:50 mixtures containing an organic acid and ammonium sulphate. Continuous lines based on empirical fits (see Table 3) are included to aid visual inspection.

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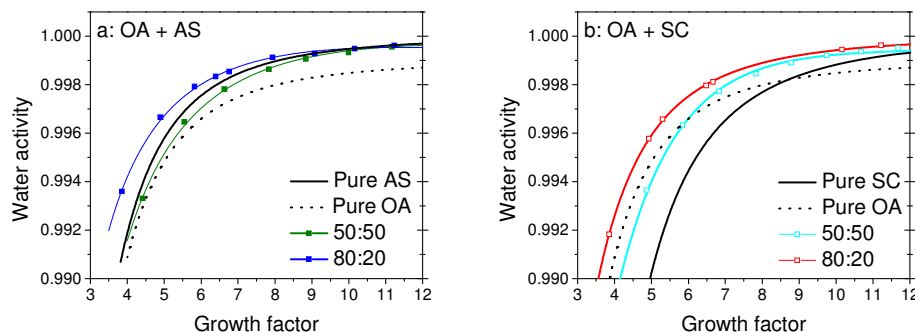


Fig. 4. (a) Measured water activity and fitted functions for the two mixtures containing oxalic acid and ammonium sulphate. (b) Measured water activity and fitted functions for the two mixtures containing oxalic acid and sodium chloride. The data is compared to parameterizations of measured water activity for oxalic acid (Varga et al., 2008) and measured water activities of ammonium sulphate or sodium chloride (Low, 1969; Young and Warren, 1992), respectively.

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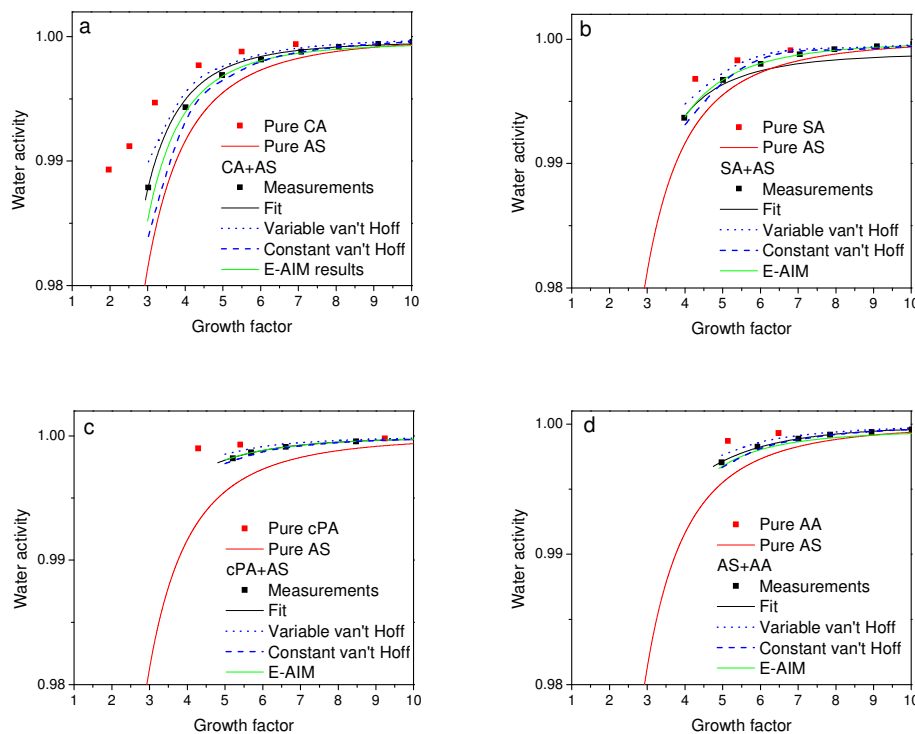


Fig. 5. Water activity of four of the studied 50:50 mixtures. The data for pure acids is obtained from Varga et al., 2007. Also shown are water activity calculated using the E-AIM model or estimated van't Hoff factor (either constant or depending on solute concentrations).

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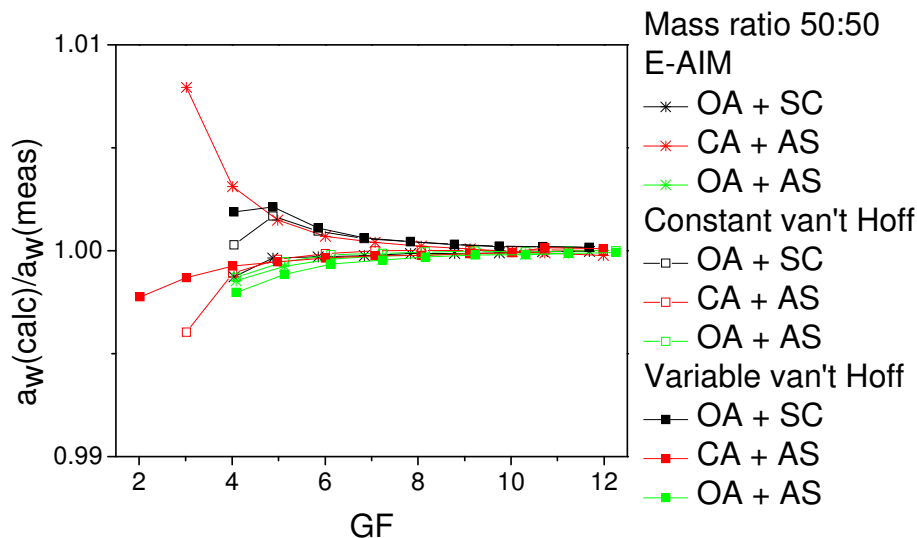


Fig. 6. The ratio between $a_w(\text{meas})$ and $a_w(\text{calc})$ calculated according to Eqs. (3) and (4) as a function of growth factor for three of the investigated mixtures with a mass ratio of 50:50. Values of $a_w(\text{calc})$ are calculated using estimated van't Hoff factors (either constant or depending on solute concentrations) or determined from the E-AIM. The measured data points are connected with straight lines to guide the eye.

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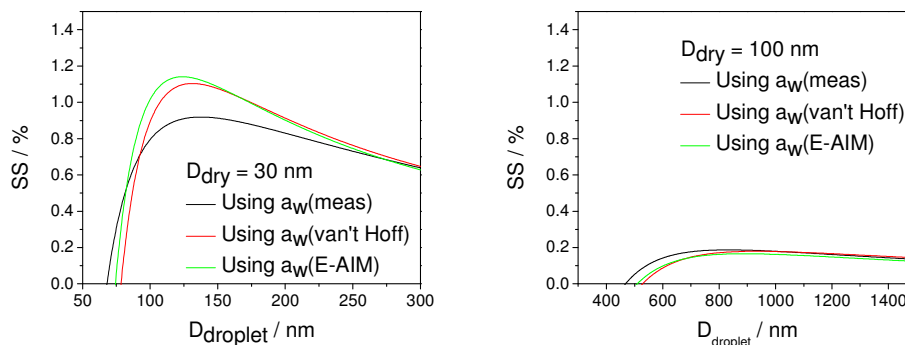


Fig. 7. Köhler curves for 50:50 mixtures of citric acid and ammonium sulphate calculated using a water activity based on either measured water activities, constant van't Hoff factors or modeled results from the E-AIM for two different dry particle diameters, D_{dry} . **(a)** $D_{\text{dry}} = 30 \text{ nm}$ and **(b)** $D_{\text{dry}} = 100 \text{ nm}$.

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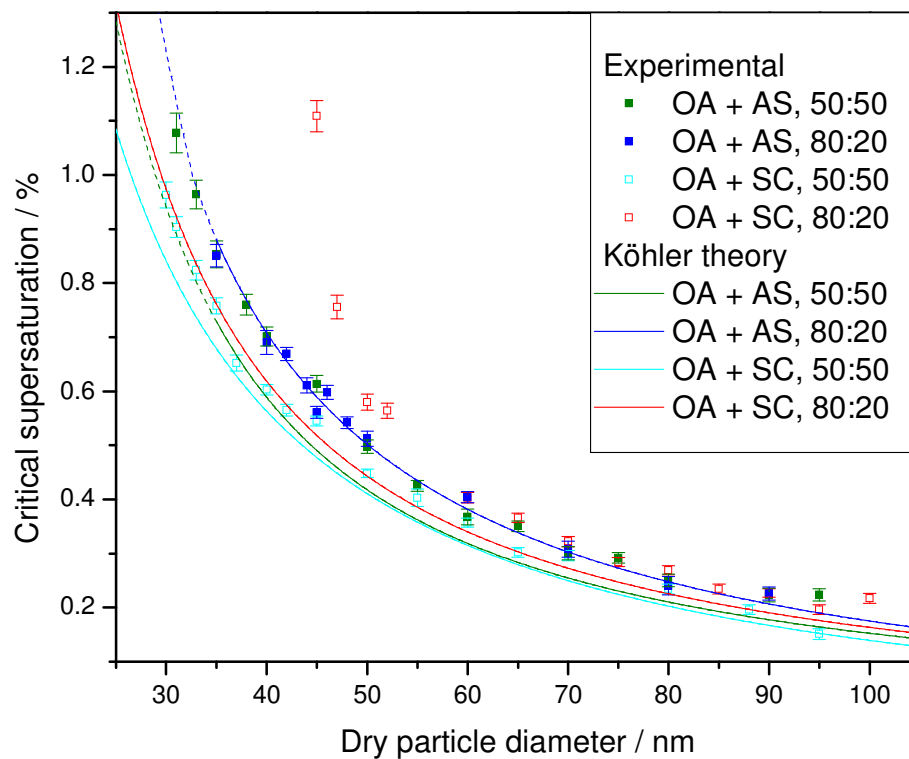


Fig. 8. Comparison between measured critical supersaturation and calculated Köhler theory for the four mixtures containing oxalic acid. The dashed sections indicate that the parameterizations of water activity are based on extrapolation.

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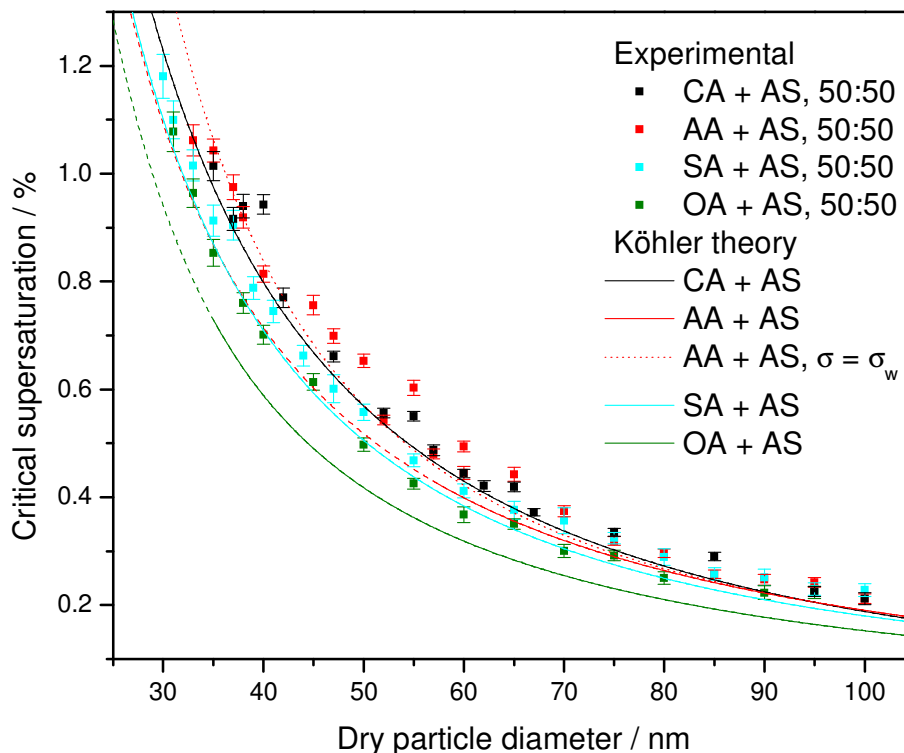


Fig. 9. Comparison between measured critical supersaturation and calculated Köhler theory for the 50:50 mixtures containing the least surface active organic compounds and ammonium sulphate. The dashed sections indicate that the parameterizations of water activity and surface tension are based on extrapolation.

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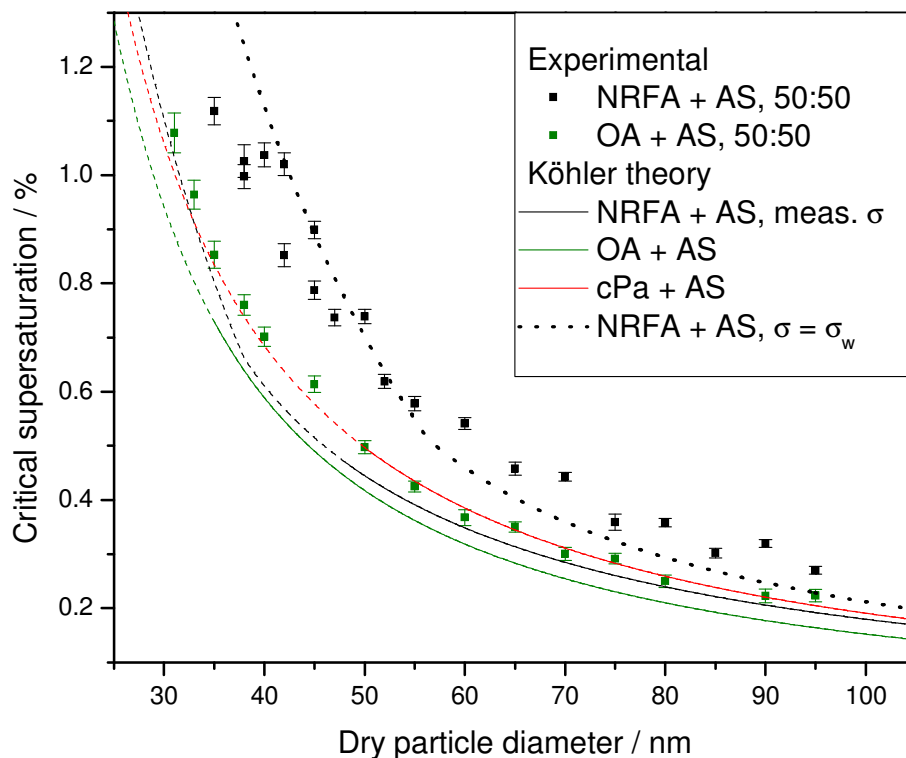


Fig. 10. Comparison between measured critical supersaturation and calculated Köhler theory for mixtures containing the most surface active organic compounds. The dashed sections indicate that the parameterizations of water activity and surface tension are based on extrapolation.

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