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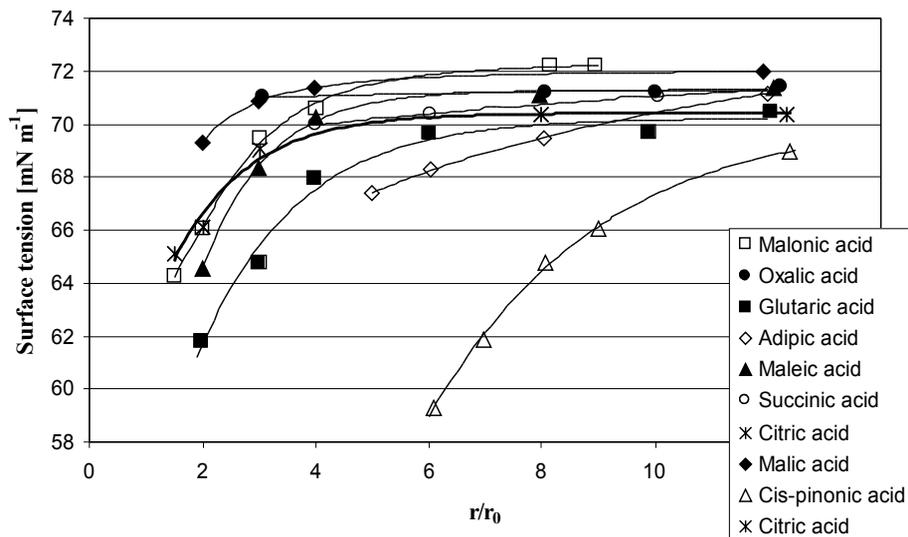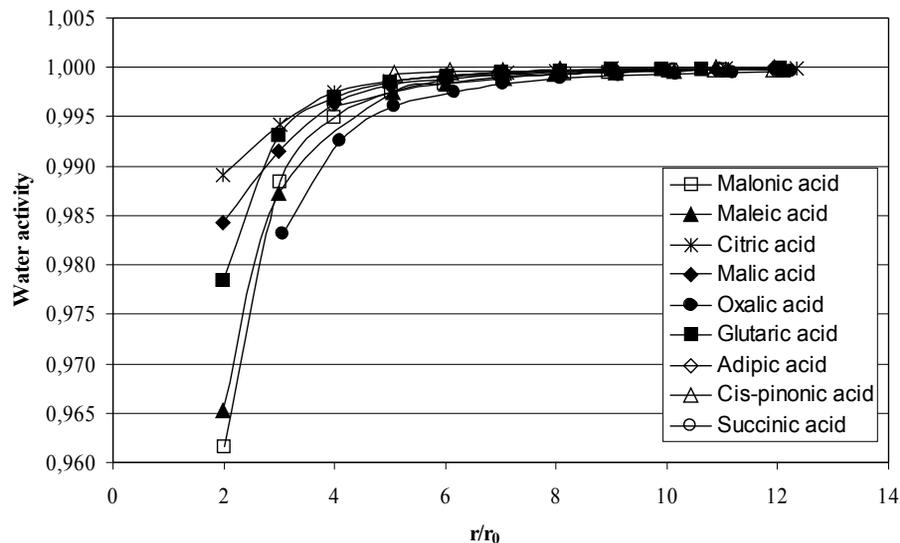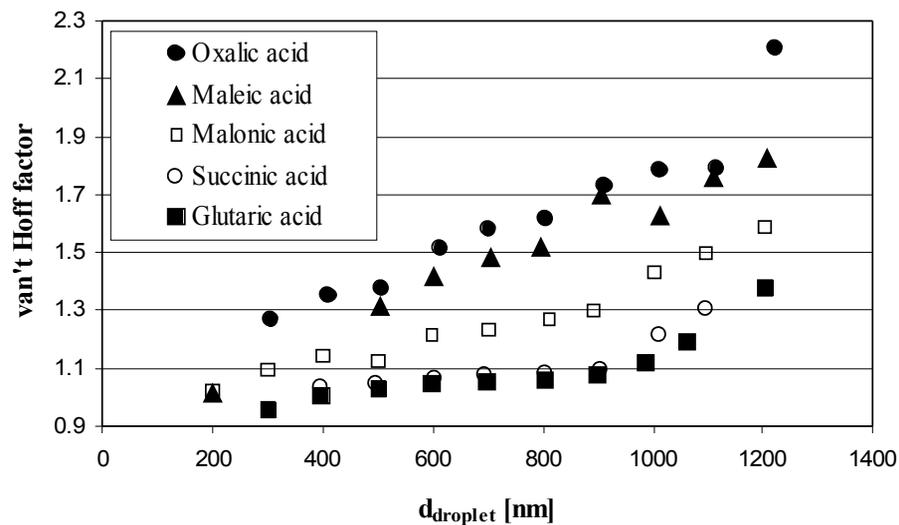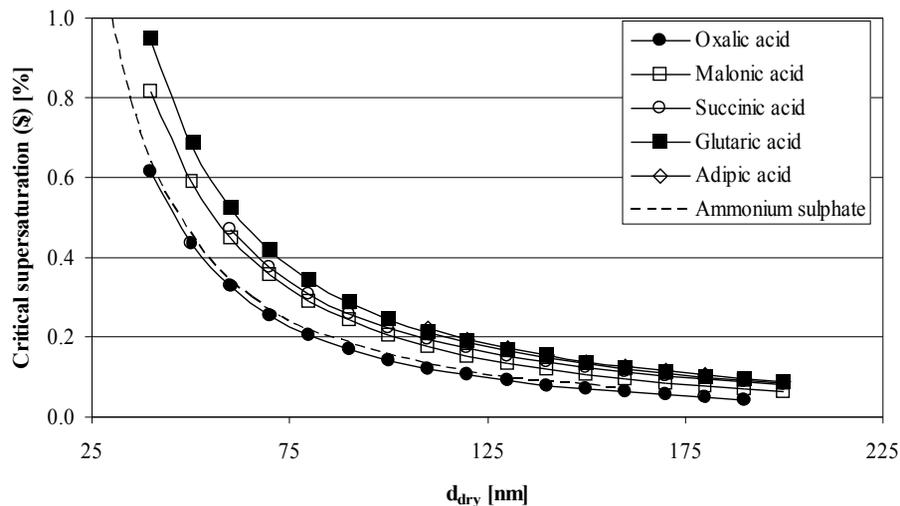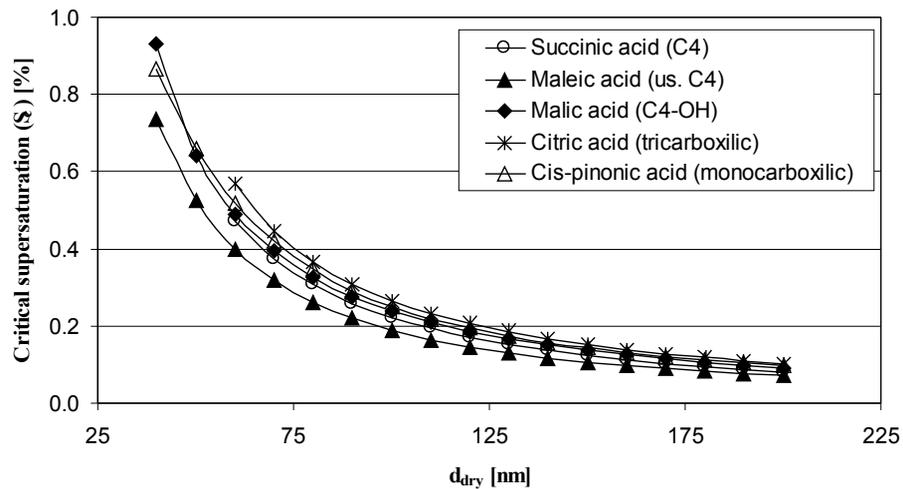
Modelling the cloud condensation nucleus activity of organic acids

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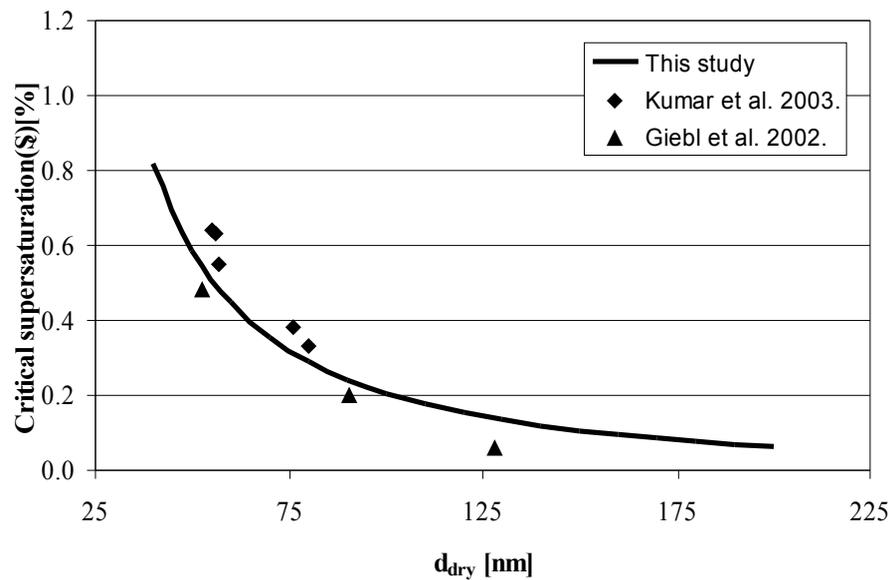
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Abstract

In this study vapour pressure osmometry was used to determine water activity in solutions of organic acids. The surface tension of the solutions was also monitored in parallel and then Köhler curves were calculated for nine organic acids (oxalic, malonic,
5 succinic, glutaric, adipic acid, maleic acid, malic acid, citric acid and pinonic acid). Surface tension depression is negligible for most of the organic acids in dilute (≤1 w/w%) solutions. Therefore, these compounds affect the supersaturation only in the beginning phase of droplet formation but not necessarily at the critical size. An exception is cis-pinonic acid which remarkably depress surface tension also in dilute (0.1 w/w%)
10 solution and hence at the critical point. The surface tension of organic acid solutions is influenced by the solubility of the compound, the length of the carbon chain and also by the polar functional groups present in the molecule. Similarly to surface tension solubility plays an important role also in water activity: compounds with higher solubility (e.g. malonic, maleic, and glutaric acid) reduce water activity significantly in the early
15 phase of droplet formation while less soluble acids (e.g. succinic and adipic acid) are saturated in small droplets and the solution starts diluting only in bigger droplets. As a consequence, compounds with lower solubility have a minor effect on water activity in the early phase of droplet formation. To deduce the total effect Köhler curves were calculated and critical supersaturations were determined for the organic acids using
20 measured surface tension and water activity. It was found that critical supersaturation grew with growing carbon number. Oxalic acid had the lowest critical supersaturation in the size range studied and it was comparable to the activation of ammonium sulfate. The S_c values obtained in this study were compared to data from CCNC measurements. In most cases good agreement was found.

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1 Introduction

The role of organic compounds in cloud formation (and thereby in indirect aerosol forcing) has received particular attention in the past few years. It has been shown that in addition to inorganic salts organic aerosol particles can also act as cloud condensation nuclei. Köhler theory is often used to calculate the critical supersaturation corresponding to an aerosol particle of known dry size and composition. However, the reliability of the calculation strongly depends on the input parameters of the model, namely the surface tension and the water activity of the solution formed on the aerosol particle. Inorganic salts of atmospheric relevance do not change the surface tension of water significantly, so in the model calculations the surface tension of water can be used. This is not the case for organic aerosol components, some of which are surfactants, e.g. humic-like substances or other organic acids. In the past few years surface tension 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., 2004) as well as that of solution of individual organic compounds (Ervens at al., 2004; Shulman et al., 1996; Tuckerman and Camega, 2004) were studied leading to a basic knowledge on their surface tension effect. However, hardly any information is available on the water activity of such atmospheric samples or model solutions of organic compounds. Consequently, the critical supersaturation of particles consisting of a pure organic compound or mixture of different components can be estimated only with high uncertainty.

Köhler theory (Köhler, 1936) predicts the supersaturation (S) of water vapour over a solution droplet of a given radius (r):

$$S = p/p_0 - 1 = a_w \exp(2\sigma M_w/(r\rho RT) - 1 \tag{1}$$

Where p is the water vapour pressure over the droplet solution, p_0 is the water vapour pressure over a flat water surface, a_w is the water activity in the droplet solution, σ is the surface tension of the droplet solution, M_w is the molecular weight of water, ρ is the density of the droplet solution, R is the universal gas constant and T is the

temperature. The vapour pressure is decreased by the dissolved matter (Raoult effect, represented by a_w) while the curvature of the droplet exerts an opposite effect (Kelvin effect, accounted for by the exponential term which is dependent on the surface tension of the solution.)

5   Water activity data for organic compounds are rare, especially for mixtures. So often the simplified form of the Köhler equation is used to calculate the critical supersaturation:

$$S = A/r - B/r^3 \qquad (2)$$

In this equation A/r represents the Kelvin effect, where $A=2\sigma M_w/\rho RT$. The second
10   term stands for the Raoult effect and B = $3i * m_s/M_s*M_w/4\pi\rho$, where m_s is the mass of the solute in the droplet, M_s is the molecular weight of the solute in the droplet, i is the van't Hoff factor of the solute in the droplet (number of species produced from 1 molecule). The van't Hoff factor is about 1 for non-electrolytes and typically higher than 1 for electrolytes. This form of the Köhler equation contains several mathematical
15   and physico-chemical simplifications, which can lead to uncertainty, especially in the early phase of droplet formation when the concentration of the solute is high. The van't Hoff factor is a critical parameter in the Raoult term since it depends on the concentration of the organic compound. Furthermore, in case of mixtures other organic and inorganic species present in the solution can also influence it. Due to the lack of infor-
20   mation on concentration dependence fixed value of van't Hoff factor is applied in most investigations to calculate the critical supersaturation. Since organic acids are weak electrolytes, van't Hoff factor of unity is often used (Raymond and Pandis, 2002; Corrigan and Novakov, 1999; Bilde and Svenningsson, 2004; Cruz and Pandis, 1997, 1998; Giebl et al., 2002; Kumar et al., 2003; Hori et al., 1996; Prenni et al., 2001). Schulman
25   et al. (1996) used 2 as van't Hoff factor for cis-pinonic acid while Mircea et al. (2002) applied i=3 for dicarboxilic acids assuming complete dissociation. In order to take into account the concentration dependence of the van't Hoff factor Kumar et al. (2003) used values between 1.2 and 2 for oxalic acid. These van't Hoff factors were derived from the dissociation constants and the actual concentration of oxalic acid in the droplet.

Thus, reasonably good agreement between theoretical calculations and experimental results were found. While this approach gives more realistic results for strong acids than a fixed van't Hoff factor, it cannot be used for mixtures of unknown compounds (e.g. atmospheric samples) since the dissociation constants are not known. In such a case, of course, also the fixed van't Hoff factor approach leads to high uncertainty.

In this paper we applied a new approach for the calculation of the Köhler curves. The osmolality and surface tension of a series of solution were measured then water activity was derived from osmolality. Finally, the original (i.e. non-simplified) form of the Köhler equation was used to calculate critical supersaturation. Thus, uncertainties originating from the use of the simplified equation were eliminated. The applicability of the method was demonstrated on organic acids, since these compounds are usually found in highest concentration in aerosol samples as individual compounds. Furthermore, model calculations and measurements with cloud condensation nucleus counters (CCNC) are available for organic acids, so the results of our model calculations can be compared to these data.

2 Experimental

In this study nine organic acids were included: oxalic, malonic, succinic, glutaric, adipic acid (C2-C6 α, ω-dicarboxylic acids), maleic acid (unsaturated C4 dicarboxylic acid), malic acid (hydroxy C4 dicarboxylic acid), citric acid (hydroxy C6 tricarboxylic acid) and pinonic acid (monocarboxylic C10 acid, oxidation product of terpene). At first solution corresponding to a defined droplet radius to dry nucleus radius were prepared. Then the osmolality was measured with a KNAUER K – 7000 vapour pressure osmometer. The working principle of the VPO is the measurement of temperature difference arising from the vapour pressure difference between a solution droplet and a pure water droplet. The VPO accounts for all processes in the solution (e.g. dissociation of solute, interactions between solute and solvent, etc.) that influence vapour pressure. Therefore, osmolality of the solutions was used to calculate water activity as described by

Kiss and Hansson (2004). An FTÅ 125 tensiometer was applied to determine the surface tension of the solutions on the basis of pendant drop shape analysis. Finally the equilibrium supersaturation was calculated with the original Köhler equation.

3 Results

3.1 Surface tension effect of organic acids

Different organic acids modify the surface tension to various extents. The effect of α, ω-dicarboxylic acids as a function of concentration (w/w%) is summarized in Table 1a. Oxalic, succinic and adipic acids, which contain even number carbon atoms, have lower solubility, therefore their effect was studied in a limited concentration range. As it can be seen in Table 1a the surface tension at 1 w/w% slightly decreases with growing hydrophobic chain (carbon number). This effect is much stronger at higher concentrations (30–40 w/w%) for the compounds containing odd number carbon atoms (malonic and glutaric acids) leading to a 10–20% decrease in surface tension. Similar effect of dicarboxylic acids was observed by Shulman et al. (1996) using the droplet volume method. For cis-pinonic acid Tuckermann and Cammenga (2004) measured similar surface tension values, for example at 0.5 w/w% they measured 57.7 mN/m which almost equals our result (57.6 mN/m).

The presence of a double bond (maleic acid) or a hydroxyl group (malic acid) in the C4 dicarboxylic acid increased the water solubility and thus enhanced the depression of surface tension in concentrated solutions as compared to the C4 α, ω-dicarboxylic acid (succinic acid) as shown in Table 1b. The effect of functional groups can be observed in the case of citric acid, too. Citric acid is a tricarboxylic acid with 6 carbon atoms and a hydroxyl group. Due to the presence of the polar functional groups its water solubility is high but the surface tension depression is moderate only (8–9%) even in high concentration (30–40 w/w%) solution. Among the organic acids studied cis-pinonic acid decreased the surface tension of the solution most efficiently (by 20%) even in a very

dilute solution (0.5 w/w%). This feature may have an important consequence during cloud formation as it will be discussed in the next paragraph.

The impact of surface tension depression on cloud droplet activation can be better assessed if surface tension is expressed as a function of droplet radius to dry nucleus

5 radius (r/r_0) as shown in Fig. 1. It can be observed that surface tension depression is negligible for most of the organic acids if $r/r_0 \geq 4$. In other words, these compounds affect supersaturation only in the beginning phase of droplet formation. An exception is cis-pinonic acid which remarkably depress surface tension also in a later phase of droplet formation ($r/r_0 \leq 10$). As a consequence, this acid is likely to decrease the Kelvin

10 term at the critical droplet size, too. However, the critical supersaturation and critical droplet size are jointly determined by the surface tension and the water activity of the solution as it is discussed in the next sections.

3.2 Water activity of organic acid solutions

Water activity of the organic acid solutions was derived from osmolality as suggested

15 earlier (Kiss and Hansson, 2004; Rosenorn et al., 2005.) The advantage of the method is that the osmometer accounts for all phenomena (e.g. dissociation of electrolytes, electrostatic interactions in solution, etc.) that influence the vapour pressure of the solution. Furthermore, the wide working range (0.005–10 mol/kg water) of the instrument allows activity measurement in the 0.85–1 activity range where the electrodynamic bal-

20 ance is less applicable. It is important to note that the accuracy of the measurement is very good, an error of 5% in osmolality results in an error of only 0.005% in water activity.

Water activity of the organic acid solutions as a function of concentration is given in Table 2. Quadratic functions with r = 0.9994–0.9998 can be fitted on the data, however,

25 for the sake of comparability activity values corresponding to the same concentration are shown in Table 2 instead of the functions. Similarly to surface tension the effect of organic acids on water activity varies from compound to compound. At a given w/w% this difference is caused by two features primarily: molecular weight (MW) and

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dissociation constant (pK) of the organic acid. Compounds with lower MW and lower pK (stronger acids) produce more ions from a given mass and, consequently, decrease water activity to higher extent. If water activity is expressed as a function of r/r_0, (Fig. 2) the density of the acid has some influence, too. A compound of higher density includes

5 more mass in a given volume, therefore results in lower water activity (assuming identical MW and K.) For example, oxalic acid (MW=90.04 g/mol, pK_1=1.23, pK_2=4.19, ρ=1900 kg/m^3) decrease water activity to 0.983 at r/r_0=3 while water activity in a glutaric acid (MW=132.12 g/mol, pK_1=4.34, pK_2=5.41, ρ=1400 kg/m^3) droplet of the same size is as high as 0.993. Similarly to surface tension solubility plays an impor-

10 tant role also in water activity: compounds with higher solubility (e.g. malonic, maleic, and glutaric acid) reduce water activity significantly in the early phase of droplet formation (r/r_0=2) while less soluble acids (e.g. succinic and adipic acid) are saturated below r/r_0=4, so these acids have constant water activity in this droplet size range and the solution starts diluting only in bigger droplets. As a consequence, compounds

15 with lower solubility have a minor effect on water activity in the early phase of droplet formation.

Water activity has been measured in some studies for malonic, oxalic, and glutaric acids. Water activity can be derived from experiments with hygroscopicity tandem differential mobility analyzer (HTDMA, Koehler et al., 2005), electrodynamic balance

20 (EDB, Peng et al., 2001), from vapour pressure measurements (Wise et al., 2003), freezing point depression (Hansen and Beyer, 2004) thermodynamic model calculations (Clegg and Seinfeld, 2005), or by fitting earlier experimental data to the van Laar equation (Gaman et al., 2004). For oxalic acid our activity values lie in the middle of the range spanned by the results by Clegg and Seinfeld (2005), Koehler et al. (2005)

25 and Peng et al. (2001) as shown in Table 2. For malonic acid our activity values have a good agreement with the results measured by Koehler et al. (2005), Hensen and Beyer (2004) and Clegg and Seinfeld (2005). Similarly, our results are in harmony with the activity data published by Clegg and Seinfeld (2005), Peng et al. (2001) and Wise et al. (2003).

As shown in Eq. (2) the simplified Köhler equation requires the van't Hoff factor (i) of the solute as an input. This introduces the largest uncertainty into the Raoult term and the calculation of saturation. The van't Hoff factor is the number of ions produced from one acid molecule. Its maximum value equals 3 for dicarboxylic acids since from one molecule 2 protons and an acid anion can be formed. However, the maximum value is reached only in infinitely dilute solutions when dissociation is complete. In more concentrated solutions the value of van't Hoff factor can be significantly less and depends on the dissociation constants of the acid. The van't Hoff factors of some organic acids in a growing droplet were calculated from the osmolality data, similarly to Sun and Ariya (2006) and are shown in Fig. 3. It can be seen that the van't Hoff factors grow with decreasing concentration as a consequence of increasing degree of dissociation. Furthermore, at a given concentration oxalic acid produces the most ions since it is the strongest acid among the compounds studied. Our results partially differ from those calculated by Sun and Ariya (2006): they obtained lower van't Hoff factor at lower concentration for malonic acid and did not see concentration dependence for malic acid. While the van't Hoff factor of oxalic and succinic acids increased with decreasing concentration, they found higher i values for succinic than oxalic acid at a given concentration which is not in agreement with the dissociation constants of the acids. It can also be observed in Fig. 3 that the actual i value in growing droplets and also around the critical size ($d_{droplet}$=550–870 nm) is significantly less than 3. The use of i=3 would result in a 2-3-fold overestimation in the magnitude of the Raoult term and thus a significant underestimation in critical supersaturation as discussed in the next paragraph.

3.3 Critical supersaturation of organic acids

Once the surface tension and water activity are known as a function of concentration (or r/r_0) Köhler curves can be calculated for a dry nucleus of a given size. The maximum value of the Köhler curve gives the critical supersaturation corresponding to an organic acid particle of that dry size. Performing the calculation for nuclei of various sizes the

critical supersaturation as a function of dry diameter can be obtained as shown for α, ω-dicarboxylic acids in Fig. 4. The critical supersaturation grows with growing carbon number. Oxalic acid which contains only two carbon atoms has the lowest critical supersaturation at each dry particle diameter. The figure also shows that for a given
5 compound the critical supersaturation decreases with growing dry diameter. Critical supersaturations for the other organic acids are shown in Fig. 5. As it can be seen, the unsaturated dicarboxylic acid (maleic acid) can activate the most easily among these compounds as a consequence of its relatively strong effect on water activity (Fig. 2) and surface tension (Fig. 1). The critical supersaturations of the other acids are very
10 similar to that of succinic acid. It is worth noting that cis-pinonic acid can activate at high supersaturation despite the fact that its surface tension lowering ability is by far the strongest among the nine acid studied (Fig. 1). This can be explained by the low water-solubility and low degree of dissociation of the acid which lead to a negligible decrease in water activity (Fig. 2). Cis-pinonic acid and oxalic acid are good examples
15 that Kelvin and Raoult effects have to be considered simultaneously. Evaluation of their CCN ability based on mere surface tension data would lead to significant under- and overestimation of critical supersaturation, respectively.

    Critical supersaturations calculated from surface tension and osmolality measurements were compared to CCNC measurements. Results for malonic and glutaric acids
20 are shown in Figs. 6 and 7. Very good agreement was found for malonic acid with CCNC measurements by Giebl et al. (2002) and Kumar et al. (2003). The situation is somewhat different for glutaric acid: while our results agreed with the CCNC results by Raymond and Pandis (2002) and Kumar et al. (2003), they were significantly lower than the CCNC data published by Cruz and Pandis (1997). Similarly, our results
25 (0.72% and 0.21%) for cis-pinonic acid particles with d_{dry}=50±9 and d_{dry}=114±23 nm are lower than those (1% and 0.3%) published by Raymond and Pandis (2002). However, it is worth noting that Raymond and Pandis gave wide confidence intervals for the CCNC data and there are no other CCNC data to compare with. So far CCNC measurements do not disprove our findings with cis-pinonic acid.

4   Conclusions

In this study solution of nine organic acids were investigated with a tensiometer and a vapour pressure osmometer to calculate their activation with the original form of the Köhler equation. Some acids with good water solubility decreased the surface tension considerably in the beginning phase of the droplet formation when the droplet solution is rather concentrated. However, the surface tension depression was negligible at low concentration corresponding to the conditions present in the droplet at activation. The only exception was cis-pinonic acid, which decreased the surface tension to 57.6 mN/m even in dilute solution (0.5 w/w%). The presence of a double bond (maleic acid) or a hydroxyl group (malic acid) in the C4 dicarboxylic acid increased the water solubility and thus enhanced the depression of surface tension in concentrated solutions as compared to the C4 α, ω-dicarboxylic acid (succinic acid). However, the dominance of polar functional groups in citric acid led to a moderate surface tension depression only even in high concentration (30–40 w/w%) solutions. Water activity of the organic acid solutions was found to be primarily determined by the dissociation constant and molecular weight of the compound: well dissociating small acids decreased the water activity most efficiently. As a consequence, oxalic acid solutions had the lowest water activity at a given concentration. It was found that among the organic acids studied oxalic acid particles activated at the lowest supersaturation despite the negligible effect on surface tension. On the other hand, cis-pinonic acid activated at high supersaturation despite the fact that its surface tension lowering ability was by far the strongest among the nine acids studied. These examples clearly show that not only the surface tension or the water activity, but the Kelvin and Raoult terms together define whether an organic compound promote or hinder activation.

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Table 1a. Surface tension values [mN m^{-1}] at different weight percents for the C2-C6 dicarboxylic acids. Oxalic, succinic an adipic acid, which contain even number carbon atom, have lower solubility, that is why there are no measured values at higher concentrations.

w/w %	Oxalic acid	Malonic acid	Succinic acid	Glutaric acid	Adipic acid
0.1	–	71.4	70.6	70.2	70.9
0.5	71.3	71.3	70.5	69.4	68.6
1	71.3	71.2	70.3	68.6	67.6
5	71.3	69.8	–	65.5	–
10	–	68.0	–	63.4	–
30	–	64.9	–	59.1	–
40	–	64.3	–	57.7	–

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Table 1b. The surface tensions [mN m^{-1}] at different mass percent for the other organic acids studied.

w/w %	Maleic acid	Malic acid	Citric acid	Pinonic acid
0.1	71.3	72.0	70.8	66.5
0.5	71.2	71.9	70.6	57.6
1	71.0	71.8	70.5	
5	68.9	71.0	69.2	
10	66.9	70.3	67.9	
30	62.4	68.4	65.1	
40	60.9	67.7	65.2	

Table 2a. The water activity values for dicarboxylic acids at different weight percents.

W/W%	Oxalic acid	Malonic acid	Succinic acid	Glutaric acid	Adipic acid
0.1	0.9995	0.9997	0.9998	0.9998	0.9997
0.5	0.9984	0.9989	0.9991	0.9992	0.9993
1	0.9971	0.9979	0.9983	0.9985	0.9987
2	0.9944	0.9960	0.9968	0.9972	–
5	0.9865 (0.982–0.99)*	0.9900	–	0.9931	–
10	–	0.9798	–	0.9867	–
20	–	0.9581	–	0.9751	–

*Range of the results by Clegg and Seinfeld (2005), Koehler et al. (2005) and Peng et al. (2001).

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Table 1. The water activity for the other organic acids studied.

W/W%	Maleic acid	Malic acid	Citric acid	Pinonic acid
0.1	0.9997	0.9998	0.9999	0.9998
0.5	0.9988	0.9992	0.9994	0.9993
1	0.9976	0.9985	0.9988	–
2	0.9954	0.9971	0.9977	–
5	0.9888	0.9927	0.9947	–
10	0.9790	–	0.9912	–
20	0.9634	–	0.9893	–

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Fig. 1. Surface tension of organic acids as a function of the droplet radius to dry particle radius.

Legend:
- □ Malonic acid
- ● Oxalic acid
- ■ Glutaric acid
- ◇ Adipic acid
- ▲ Maleic acid
- ○ Succinic acid
- ✳ Citric acid
- ◆ Malic acid
- △ Cis-pinonic acid
- ✳ Citric acid

Y-axis: Surface tension [mN m^{-1}]

X-axis: r/r_0

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Fig. 2. Water activity of organic acids as a function of droplet radius to dry particle radius.

Fig. 3. Van't Hoff factors of organic acids in a droplet formed on a dry particle of 100 nm in diameter.

Fig. 4. Critical supersaturation as a function of dry particle diameter for the 5 α, ω-dicarboxylic acids studied.

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Fig. 5. Critical supersaturation as a function of dry particle diameter for the other organic acids studied.

Fig. 6. Comparison of our results for malonic acid with CCNC data.

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Fig. 7. Comparison of our results for glutaric acid with CCNC data. Data near the points means the confidence interval for results of Cruz and Pandis (1997) and Raymond and Pandis (2002).

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