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and inorganics as
CCN**

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Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt

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Abstract

Critical supersaturations for internally mixed particles of adipic acid, succinic acid and sodium chloride were determined experimentally for dry particles sizes in the range 40–130 nm. Surface tensions of aqueous solutions of the dicarboxylic acids and sodium chloride corresponding to concentrations at activation were measured and parameterized as a function of carbon content. The activation of solid particles as well as solution droplets were studied and particle phase was found to be important for the critical supersaturation. Experimental data were modelled using Köhler theory modified to account for limited solubility and surface tension lowering.

1. Introduction

Atmospheric aerosols affect global climate directly via interaction with electromagnetic radiation (e.g. [Andronova et al., 1999](#); [Jacobson, 2001](#); [Houghton et al., 2001](#)) and indirectly via their role in cloud formation and importance for cloud droplet number and cloud optical properties ([Albrecht, 1989](#); [Hansen et al., 1997](#); [Rosenfeld and Woodley, 2000](#); [Lohmann, 2002](#); [Liepert et al., 2004](#)).

The ability of an aerosol particle to become a cloud droplet depends on the chemical composition and physical properties of the particle and only a fraction of all particles are able to grow into cloud droplets under atmospheric conditions. Aerosol particles that can grow into cloud droplets (activate) under atmospheric supersaturations are cloud condensation nuclei (CCN). The supersaturation needed to activate the particles is called critical supersaturation.

In the atmosphere particles may be solid or liquid, they may exist as solution droplets or even as multiphase systems (e.g. [Prenni et al., 2001](#); [Brooks et al., 2003](#); [Marcolli et al., 2004](#)). Furthermore, particles may go from one phase to the other during cloud processing. Recently it has been suggested and experimentally verified that particle phase plays a major role for the activation of particles consisting of slightly soluble

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organic compounds (Bilde and Svenningsson, 2004; Hori et al., 2003; Broekhuizen et al., 2004). In the atmosphere particles are most likely to be mixtures of organic and inorganic components. Even if a purely organic particle exists it is likely to collect inorganic material during cloud processing. While some data on the cloud droplet activation of pure (e.g. Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Prenni et al., 2001; Raymond and Pandis, 2002; Kumar et al., 2003) and multi-component solid particles have recently appeared (e.g. Cruz and Pandis, 1998; Hegg et al., 2001; Raymond and Pandis, 2003; Kumar et al., 2003) few such data on multi-component solution droplets have been reported (Broekhuizen et al., 2004).

In this work the importance of particle phase for cloud droplet activation of multi-component particles containing inorganic as well as organic compounds is therefore addressed. As representative of inorganic aerosol components the ubiquitous salt sodium chloride was chosen. As organic components adipic and succinic acid were chosen, which have been identified as common compounds in the water-soluble fraction of organic aerosols (Saxena and Hildemann, 1996). These acids are known to be moderately surface active and as discussed in recent papers (Facchini et al., 1999; Shulman et al., 1996) this can affect the critical supersaturation of atmospheric aerosol particles, but experimental data and parameterizations of relevant drop surface tensions are rare. Therefore surface tension measurements of the mixtures at relevant concentrations were conducted, parameterized as a function of the carbon content of the individual acids and incorporated in a Köhler model taking into account limited solubility. It has recently been suggested (Li et al., 1998; Sorjamaa et al., 2004) that partitioning of surface active organic compounds between bulk and surface in activating droplets affects the critical supersaturation. But this effect is expected to be strongest for highly surface active species and is therefore not taken into account herein.

2. Theory

Two competing effects determine the vapor pressure of water over an aqueous solution droplet: the solution effect (Raoult's law) which tends to decrease vapor pressure and the curvature (Kelvin) effect which tends to increase the vapor pressure. The vapor pressure of water over an aqueous solution droplet relative to that over a flat surface is given by the Köhler equation (Köhler, 1936):

$$S = \frac{p}{p_0} = a_w \cdot \exp\left(\frac{4M_w\sigma}{RT\rho_w D_{pw}}\right) \quad (1)$$

a_w is the water activity, D_{pw} is droplet diameter, M_w is the molar weight of water, σ is the air-liquid surface tension, R is the gas constant, T is temperature and ρ_w is the density of water. The Raoult term in classical Köhler theory applies only for completely soluble substances whereas recent modifications take limited solubility into account (Shulman et al., 1996; Kulmala et al., 1997; Laaksonen et al., 1998). For a droplet containing several species the water activity can be approximated by:

$$a_w = \frac{n_w}{n_w + \sum_i \nu_i n_i} \quad (2)$$

n_i is the number of moles of compound i , ν_i is the van't Hoff factor and n_w number of moles water (Pruppacher and Klett, 1997).

By assuming that compound i is homogeneously distributed in the aqueous phase and that its concentration is determined by its water solubility only the number of moles of compound i in a multicomponent solution droplets can be expressed as:

$$n_i = \text{Min} \left\{ \frac{(D_{pw}^3 - d_0^3) \cdot C_{\text{sat}}}{M_i}, \frac{\beta_i \cdot \rho_0 \cdot d_0^3}{M_i} \right\} \cdot \frac{\pi}{6} \quad (3)$$

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where β_i is the mass fraction of compound i in the initial dry particle of diameter d_0 and C_{sat} is the water solubility of compound i (mass per volume). Assuming additivity of volumes the density of the dry particle ρ_0 is given as:

$$\frac{1}{\rho_0} = \sum_i \frac{\beta_i}{\rho_i} \quad (4)$$

5 Water solubilities of 25 g l^{-1} and 88 g l^{-1} were used for adipic and succinic acid, respectively (Saxena and Hildemann, 1996). A van't Hoff factor of 1 and 2 was used for organic acid (Kiss and Hansson, 2004) and NaCl, respectively.

As predicted by Shulman et al. (1996) the Köhler curve obtained using modified Köhler theory has up to three maxima (Fig. 1). The cusps represent the points where
10 adipic and succinic acid respectively are completely dissolved. The maximum at the highest wet diameter represents a solution droplet were all components are dissolved. Therefore the corresponding supersaturation is identical with that obtained by assuming that the organic acids are infinitely soluble in water (classical Köhler theory). The supersaturations corresponding to the first two maxima may in some cases be higher
15 than the critical supersaturation obtained from traditional Köhler theory and as explained in Bilde and Svenningsson (2004) they can be viewed as an activation barrier which is due to the presence of a undissolved solid core of organic acid(s). This barrier is eliminated when the activating particle starts out as a solution droplet. The magnitude of the first two maxima may be dramatically influenced by the presence of small
20 amounts of soluble material whereas the third maxima is less influenced.

3. Experimental

Aqueous solutions of two dicarboxylic acids (adipic acid, Riedel-de Haën, purity $\geq 99.8\%$; succinic acid, Merck, purity $>99.5\%$) and sodium chloride (Riedel-de Haën, purity $>99.8\%$) in three different proportions (mix. 1: 93% adipic acid (aa), 5% succinic acid (sa), 2% sodium chloride (NaCl); mix. 2: 80% aa, 18% sa, 2% NaCl; mix. 3: 5%

aa, 93% sa, 2% NaCl) were prepared. To avoid impurities all glassware was cleaned with purified water (MilliQ) and all solutions were prepared with commercial available ultra pure water (Fluka, 7732-18-5).

3.1. Surface tension measurements

5 Surface tensions of the water-organic-inorganic salt systems were performed with the De Nöuy method (De Nöuy, 1919; Freud and Freud, 1930) over the temperature range 273–306 K.

The apparatus consists of a De Nöuy tensiometer (Krüss GmbH, Hamburg, Instrum. Nr. K6, type 90331), a Platinum-Iridium ring of radius r , and a glass vessel for the solutions. For measurement a Pt-ring is pulled through the liquid/air interface and the maximum downward force directed to the ring is measured. The surface tension is determined by

$$\sigma = \frac{P}{4\pi r} F \quad (5)$$

15 where P is the detachment force and F is a dimensionless correction factor determined experimentally (Harkins and Jordan, 1930). The temperature was controlled to within ± 0.3 K either by a regulated stream of cold nitrogen through a double-walled beaker containing the mixtures or by a warm water bath.

The instrument was tested before every measurement serie using ion-exchanged, doubly distilled water as standard. The result found for water ($72.49 \text{ mNm}^{-1} \pm 0.82 \text{ mNm}^{-1}$ at 295 K) agrees well with the literature value (72.75 mNm^{-1} at 293 K, Vargaftik et al., 1983) and the temperature dependent parametrization given by Pruppacher and Klett (1997) (72.50 mNm^{-1} at 295 K).

3.2. CCN-measurements

25 Aerosol particles were generated by atomizing aqueous solutions in a constant output atomizer (TSI, 3076) and their ability to act as cloud droplets was studied in a static

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thermal gradient diffusion chamber (CCNC, University of Wyoming, CCNC-100B). The number of activated particles is detected via light scattering. A similar CCNC and the calibration of it has been described in [Delene and Deshler \(2000\)](#).

The instruments supersaturation was calibrated using dry monodisperse NaCl and $(\text{NH}_4)_2\text{SO}_4$ particles over the supersaturation range of 0.2–2%. Theoretical values were calculated via Köhler Theory as described above. The resulting calibration equation ($R^2=0.9959$) was applied to all experimental data.

Two types of experiments were performed: 1) dry measurements where the aerosol particles were dried before entering the cloud chamber and 2) wet measurements, where the particles entered the cloud chamber as solution droplets supersaturated in respect to the organics but subsaturated in respect to sodium chloride.

For the dry measurements (Fig. 2a) the generated aerosol was dried to relative humidities in the range 1–20% using diffusion dryers and a specific diameter was selected using a differential mobility analyzer (DMA, TSI, 3080). Particles generated in this way are referred to as initially dry particles. Downstream the DMA the CCNC was used to determine the particles critical supersaturation. Particle number was measured as a reference with a particle counter (TSI, CPC 3010).

Studies of evaporation rates of adipic and succinic acid ([Bilde et al., 2003](#)) show that evaporation over the time scale particles spend in the tubing in these experiments is negligible. This was confirmed by comparing the particle size selected by the first DMA to their size just before entering the CCNC.

In the set-up for the wet measurements (Fig. 2b) the diffusion dryers were bypassed and the particles entered the DMA wet. The sheath air of the DMA was humidified to 70%. The monodisperse aerosol exiting the DMA was divided into two streams. One stream was kept at the humidity of 70% until entering the cloud chamber. The other stream was dried and the dry particle size was measured using a scanning mobility particle analyzer (TSI, SMPS 3934) consisting of a DMA and a CPC.

Throughout this work the supersaturation in the CCNC was varied between 0.2 and 2% for a fixed dry or dry adequate particle diameter in dry and wet experiments, re-

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spectively. The activated particle fraction, the number of CCN normalized to the total particle number (CN), is ideally a step function. In reality the step is not always very steep (Fig. 3). By choosing a particle diameter via DMA technique a quasi monodisperse aerosol distribution is selected. The width of this distribution is dependent on the aerosol to sheath air flow ratio in the DMA and influences the slope in a plot of activated fraction versus supersaturation (e.g. Fig. 3). This was considered by fitting the data to a function taking the DMA transfer function into account. The critical supersaturation is the point of 50% activation.

4. Results and discussion

Three different mixtures containing adipic acid, succinic acid and sodium chloride were investigated with respect to surface tension and activation behavior. The mass fraction of the inorganic salt was kept at 2% and the relative amounts of adipic and succinic acid were varied.

4.1. Surface tension of mixtures

To investigate surface tensions in the relevant concentration range, drop concentrations at activation were estimated using Köhler theory accounting for limited solubility. Surface tension measurements were performed using solutions corresponding roughly to the concentrations at activation of initially dry particles with diameters of 40, 50 and 100 nm. The exact concentrations studied are given in Table A1.

A linear temperature dependence was found for all three mass mixing ratios of adipic acid, succinic acid and NaCl with water (Fig. 4). Slopes, offsets and errors of the linear least square fits are given in Fig. 4.

In Fig. 4a the solute concentration is very close to the solubility limit of adipic acid for the studied solutions and the surface tension is therefore similar for both solutions.

Pure adipic acid is found to be more surface active than pure succinic acid (Shulman

et al., 1996; Dash and Mohanty, 1997) and consistently a stronger surface tension lowering is observed with increasing adipic acid concentration in the solution.

According to Facchini et al. (1999) surface tension lowering of atmospheric water samples can be described by the Szyszkowski-Langmuir equation:

$$\sigma = \sigma_w(T) - aT \ln(1 + bC) \quad (6)$$

where C is the concentration of soluble carbon given in moles of carbon per kg of water. Applying Eq. (6) to multiple mixtures, it is required that the coefficients a and b are determined from experimental data for all mixing ratios investigated. A modification of this equation has been tested and proven successful for all mixtures studied herein.

$$\sigma = \sigma_w(T) - \sum_i \chi_i a_i T \ln(1 + b_i C) \quad (7)$$

Equation (7) allows calculation of the surface tension of mixtures at the temperature T on the basis of the coefficients a_i , b_i for the pure compounds fulfilling Eq. (6) and χ_i , the carbon content of compound i (C_i in moles of carbon per kg of water) in respect to the total soluble carbon C in solution:

$$\chi_i = \frac{C_i}{C} \quad (8)$$

Recently Kiss et al. (2004) have shown that high concentrations of inorganic salts can enhance surface tension lowering of HULIS. Due low inorganic salt concentrations of the here investigated mixtures this effect was assumed to be negligible.

Values for a_i and b_i of pure adipic acid were derived by fitting Eq. (6) to data points given by Shulman et al. (1996) (Table 1). Fitting coefficients for pure succinic acid are taken from Svenningsson et al. (2004)¹.

¹Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic Growth and Critical Super-saturations for Mixed Aerosol Particles of Inorganic and Organic Compounds of Atmospheric Relevance, to be submitted, 2004.

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Predicting surface tensions for the experimentally investigated solutions applying this approach leads to a good agreement (Fig. 5, $R^2=0.956$) in the here considered temperature ($273\text{ K}\leq T\leq 306\text{ K}$) and concentration range ($0.25\text{ mol kg}^{-1}\leq[C]\leq 3.06\text{ mol kg}^{-1}$). In general, mixtures close to the solubility limit were difficult to measure due to beginning precipitation. The precipitated compounds were resoluted by heating the solution, followed by cooling and immediate surface tension measurement. This procedure might explain the deviation from the 1:1 line in Fig. 5 for low surface tensions.

More work is needed to show if Eq. (7) is applicable for other organic compounds and for higher concentration of inorganic material.

4.2. Cloud droplet activation

Critical supersaturations for initially dry particles were in the range between 1.3% (60 nm, highest share of slightly soluble organics) and 0.16% (110 nm, lowest share of slightly soluble organics, Fig. 6) For solution droplets the critical supersaturation was in general lower and the difference between the mixtures was not as strong. The experimental values range between about 1% supersaturation (40 nm) and 0.18% (130 nm).

To activate the initially dry particles here investigated the critical supersaturation has to be considerably higher than for e.g. pure sodium chloride particles of the same size. In comparison with a pure salt particle of 60 nm, which requires a supersaturation of 0.22% to activate, the critical supersaturation has to be 6×, 4× and 2× as high for the studied initially dry particles, respectively (in order of decreasing share of adipic acid in the particle).

The mixed particles exhibit a significant difference in required supersaturation between initial dry particles (when a solid core is present) and solution droplets and the difference gets stronger with increasing mass fraction of the less soluble organic acid. The solution droplets, obtained via the wet set-up (Fig. 2b), do not have to overcome the above described solubility barriers and can therefore easier activate than the dry particles.

The experimentally determined critical supersaturation values (Fig. 6: $S_{c,\text{exp}}^{\text{dry/wet}}$)

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were on one hand compared to theoretical values obtained by neglecting the surface tension lowering (Fig. 6: $S_{c,theo}^{dry/wet}, \sigma_w(T)$) and on the other hand to a Köhler theory applying the solutions surface tension calculated at activation via the parametrization explained above (Fig. 6: $S_{c,theo}^{dry/wet}, \sigma(T, C)$). Both theories take limited solubility into account.

For wet particles measured values and theory taking the parameterized surface tension of the solution into account agree very well for all mixture types. In case of dry particles another effect seems to dominate the lowering of surface tension and the particles activate at a higher critical supersaturation than predicted.

However, in mixtures with a high share of adipic acid the difference between the theories applying more and less realistic surface tensions pales in comparison with the difference between the wet and dry activation state. E.g. for a 60 nm particle consisting of 93% adipic acid, 5% succinic acid, 2% sodium chloride the deviation between the difference surface tension approaches is 18% and 13% for a dry and wet particle, respectively, while there is a 43% discrepancy between initial dry and wet particles. An equal sized particle containing 5% adipic acid, 93% succinic acid, 2% sodium chloride activates at the same supersaturation in wet and dry state, whereas the difference in surface tension accounts for 3% difference in critical supersaturation.

5. Conclusions

Surface tensions of mixtures of two slightly soluble organic acids and an inorganic salt were measured and parameterized as a function of carbon content of the individual acids and temperature. It was found that the actual surface tension of the droplet at activation is dependent on the mole fraction of both acids.

Including surface tension lowering in Köhler theory taking limited solubility into account describes the activation behavior of the solution droplets well, but when a solid core is present theory underestimates critical supersaturation.

Even more crucial than surface tension for the here studied mixtures is the phase

state of the particles. It was shown above that dry particles need much higher supersaturation to activate than their wet solution droplet counterpart. Knowledge of the phase state is therefore crucial otherwise an error in critical supersaturation of more than 50% can be made and thereby in predicting the CCN number.

5 *Acknowledgements.* This work is supported by the Swiss National Science Foundation, the Danish Natural Science Research Council and the Nordic Center of Excellence, Research Unit BACCI.

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Table 1. Coefficients a_i and b_i of pure adipic acid and succinic acid derived by fitting Eq. (6) to N data points.

compound	N	a_i	b_i
succinic acid	6	0.0264	0.286
adipic acid	4	0.0106	11.836

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Table A1. Mass of adipic acid (aa), succinic acid (sa), sodium chloride (NaCl) and water in each individual solution used for surface tension measurements. Concentrations correspond roughly to the point of activation of initially dry particles at different dry diameters d_0 .

d_0 nm	m_{aa} g	m_{sa} g	m_{NaCl} g	m_{water} g
93% aa, 5% sa, 2% NaCl				
100	2.257	0.674	0.271	96.954
50	2.016	1.337	0.535	96.129
80% aa, 18% sa, 2% NaC				
100	0.770	0.175	0.019	99.038
50	2.192	2.393	0.264	95.305
5% aa, 93% sa, 2% NaCl				
100	0.036	0.674	0.015	99.294
50	0.106	1.860	0.040	98.005
40	1.742	6.135	0.947	91.219

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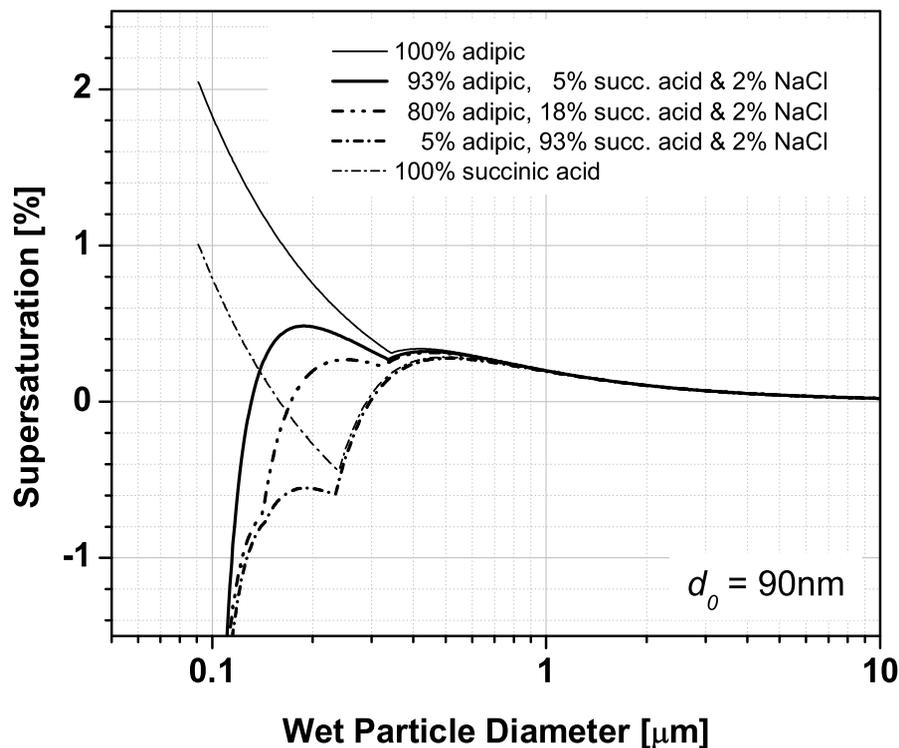


Fig. 1. Köhler curves accounting for limited solubility for initially dry particles with a diameter of 90 nm of ternary mixtures of adipic and succinic acid and sodium chloride. For comparison the curves for pure adipic and succinic acid are also given.

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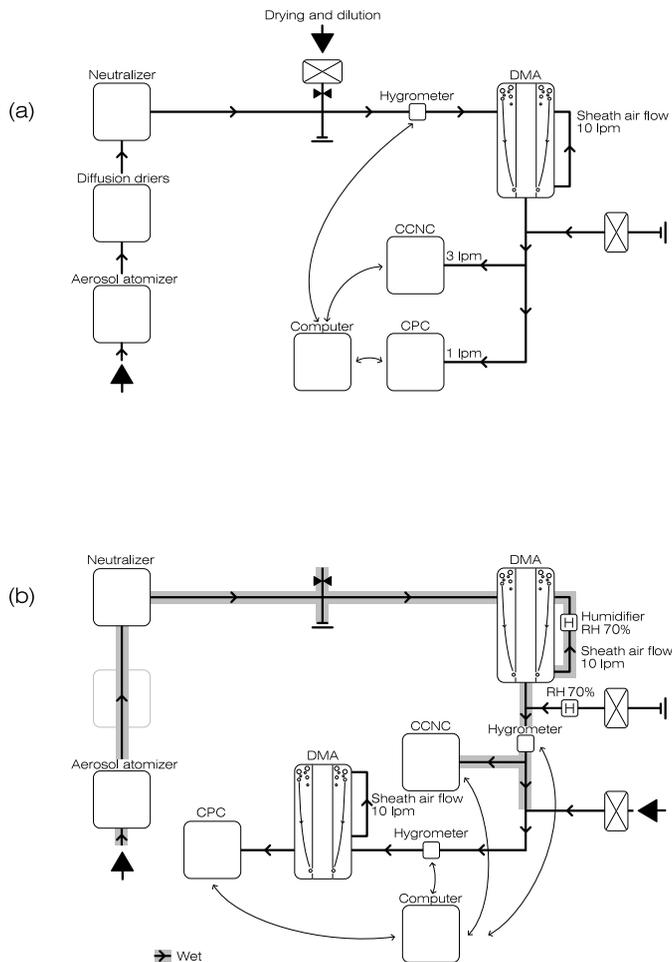


Fig. 2. Experimental setup of CCNC measurements for **(a)** initially dry particles and **(b)** solution droplets. In **(b)** the grey highlighted lines show the pathway of the wet kept particles.

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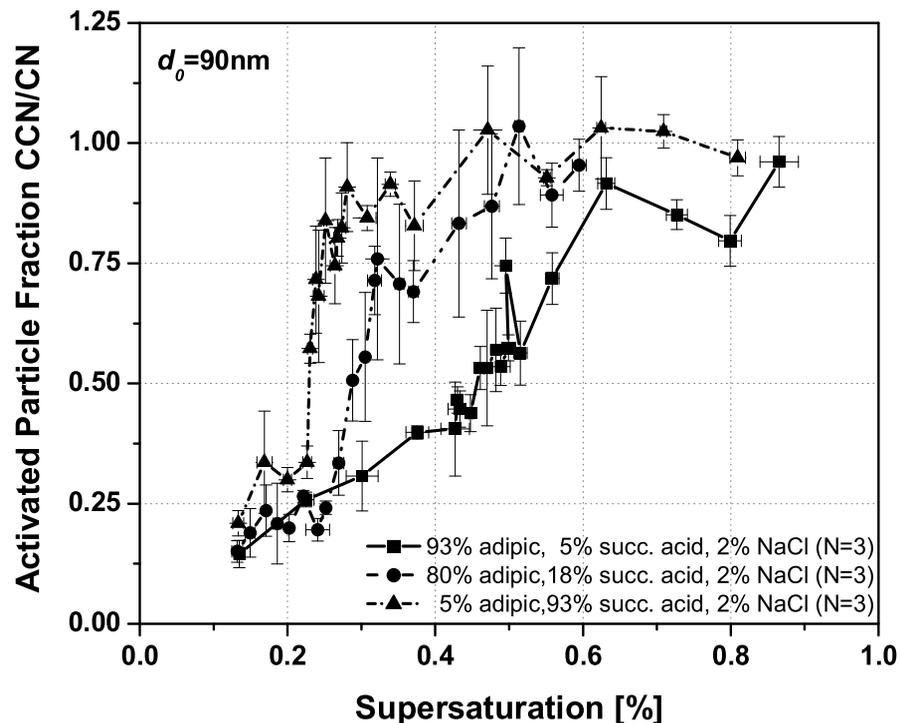


Fig. 3. Example of activation measurements for ternary mixtures of adipic and succinic acid at a dry particle diameter $d_0 = 90$ nm. N is the number of scans included in the average and the bars give the standard deviation of the measurements.

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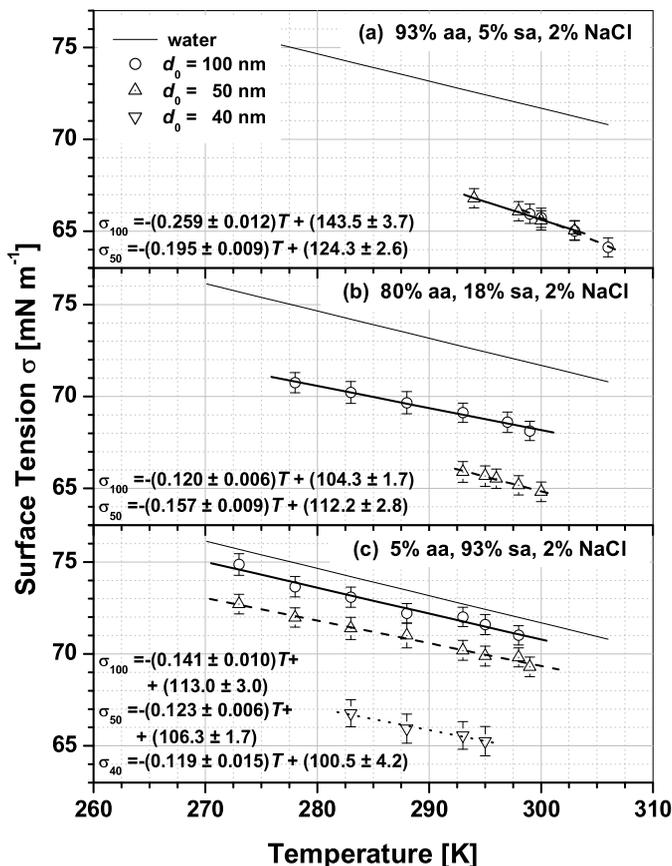


Fig. 4. Experimentally determined surface tensions of ternary mixtures of adipic and succinic acid including NaCl in water. Solution concentrations corresponding roughly to the concentration at activation for initially dry particles with diameters of 40, 50 and 100 nm, respectively. Error bars represent a combined error of: relative error from the instrumentation ($\pm 0.3\%$), uncertainty in temperature controlling system (± 0.3 K), $\pm 0.3\%$ of the mass fraction and standard deviation from fit ($\pm 0.3\%$).

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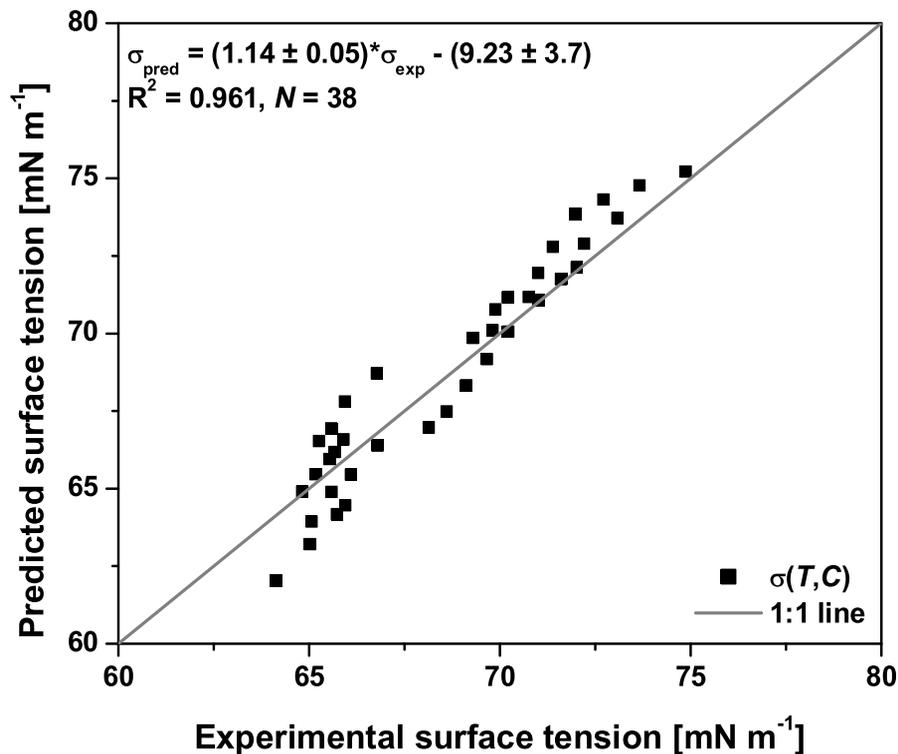


Fig. 5. Predicted surface tensions of mixtures containing dicarboxylic acids and sodium chloride using Eq. (7) versus experimental derived surface tensions in a temperature range of $273\text{ K} \leq T \leq 306\text{ K}$ and a total soluble carbon concentration in water of $0.25\text{ mol kg}^{-1} \leq [C] \leq 3.06\text{ mol kg}^{-1}$.

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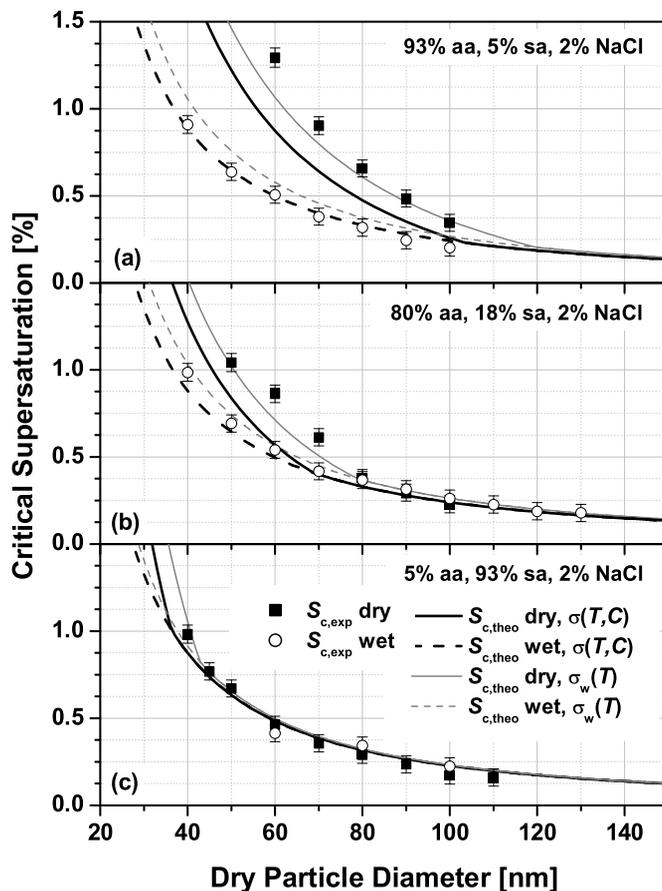


Fig. 6. Comparison of critical supersaturation as a function of particle size for initial dry (solid lines) and wet (dashed lines) particles of ternary mixtures of adipic acid, succinic acid and sodium chloride. Lines were obtained from modified Köhler theory at $T=298$ K, symbols are experimental results. The experimental uncertainty was calculated based on supersaturation calibration data.

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