Tellus (2004), 56B, 128–134
Printed in UK. All rights reserved

TELLUS

CCN activation of slightly soluble organics: the importance of small amounts of inorganic salt and particle phase

By MERETE BILDE* and BIRGITTA SVENNINGSSON, *University of Copenhagen, Department of Chemistry, Universitetsparken 5, DK-2100 Copenhagen, Denmark*

(Manuscript received 26 February 2003; in final form 15 August 2003)

ABSTRACT

Using a static thermal-gradient diffusion cloud condensation nucleus chamber we study the effect of small amounts of inorganic salts on the cloud droplet activation of two slightly soluble organic aerosol components (adipic and succinic acid) and experimentally confirm the two maxima predicted by Köhler theory modified to take limited solubility into account. Equally importantly we suggest (and confirm experimentally) that solid and liquid (supersaturated) particles of slightly soluble organic compounds follow two different Köhler curves and that knowledge about the particle phase and thereby the humidity history is important for interpretation of experimental data and modelling of the aerosol indirect climate effect.

1. Introduction

Aerosols influence global climate directly by scattering radiation as well as indirectly via their role as cloud condensation nuclei, affecting cloud optical properties (IPCC, 2001). Slightly soluble organic compounds constitute a significant fraction of atmospheric aerosols (Saxena and Hildemann, 1996) and pioneering laboratory work on organic particles has suggested that slightly soluble organic substances influence the activation of particles to cloud droplets and thereby the aerosol indirect climate effect (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Prenni et al. 2001; Raymond and Pandis, 2002). Even so, the microphysics underlying the role of slightly soluble organic compounds in cloud formation is not well understood and experimental laboratory data do not always agree with theory in the form of the modified Köhler equation (Shulman et al. 1996). For example succinic acid, $HOOC(CH_2)_2COOH$, has been found to activate according to traditional Köhler theory as though it is infinitely soluble (Corrigan and Novakov, 1999; Prenni et al. 2001) even though modified Köhler theory predicts a higher critical supersaturation and adipic acid, $HOOC(CH_2)_4COOH$, apparently obeys neither traditional nor modified Köhler theory and results reported in the literature from different studies of adipic acid (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Raymond and Pandis, 2002) are not consistent. To close the gap between experimental results and microphysical understanding as described by modified Köhler theory we therefore focus on adipic and succinic acid. We show that small amounts of salt have a dramatic effect on the critical supersaturation of these slightly soluble organic aerosol components and experimentally confirm the two maxima predicted by Köhler theory modified to take limited solubility into account. Furthermore, we show that solid and liquid particles follow two different Köhler curves and suggest that knowledge concerning particle phase and humidity history is important for interpretation of experimental data and modelling of the aerosol indirect climate effect. Modified Köhler theory accounts for a number of effects, including limited solubility and surface tension lowering. In this work we focus on solubility only and in the following modified Köhler theory refers to the modification introduced by limited solubility.

2. Theory

Traditional equilibrium Köhler theory (Köhler, 1936), describes the activation of inorganic salts to cloud droplets. To account for the presence of a non-dissolved core of organic material Shulman et al. (1996) and later Laaksonen et al. (1998) and Kulmala et al. (1997) modified the original Köhler equation to include both a slightly soluble organic compound and an inorganic salt. Modified Köhler theory gives the saturation ratio of water, S, over a solution droplet relative to a flat pure water surface as

$$S = \gamma_W x_w \exp\left(\frac{4 M_w \sigma}{R T \rho D_p}\right). \tag{1}$$

---

*Corresponding author.
e-mail: mbilde@kiku.dk

The first term represents water activity (Raoults law) as the product of the water activity coefficient γ_{w} and the mole fraction of water, x_{w}. The exponential term represents the Kelvin effect as a function of droplet diameter, D_p. M_{w} is the molar weight of water, σ is the air–liquid surface tension, R is the gas constant, T is the temperature and ρ is the density of the solution droplet. The mole fraction of water is expressed as

$$x_{\mathrm{w}} = \frac{n_{\mathrm{w}}}{n_{\mathrm{w}} + \upsilon_{\mathrm{s}} n_{\mathrm{s}} + \upsilon_{\mathrm{ss}} n_{\mathrm{ss}}} \tag{2}$$

where the subscripts s, ss and w denote salt, slightly soluble organic and water, respectively. n_j and ν_j are the number of moles and number of ions into which compound j dissolves. The number of moles of slightly soluble organic compound in solution is limited by the water solubility of the compound. Until enough water to dissolve all organic material has condensed on the particle there is an undissolved core of organic material. n_{ss} can be expressed as

$$n_{\mathrm{ss}} = \min\left[\frac{\left(D_p^3 - d_0^3\right) C_{\mathrm{sat}}}{M_{\mathrm{ss}}}, \frac{\beta \rho_0 d_0^3}{M_{\mathrm{ss}}}\right] \frac{\pi}{6} \tag{3}$$

where β is the mass fraction of slightly soluble organic material in the initial dry particle of diameter d_0 and C_{sat} is the solubility of the slightly soluble compound (mass per volume). Assuming additivity the density of the dry particle ρ_0 is given as

$$\frac{1}{\rho_0} = \frac{1-\beta}{\rho_{\mathrm{s}}} + \frac{\beta}{\rho_{\mathrm{ss}}}. \tag{4}$$

When all organic material is dissolved eq. (1) is equal to the traditional Köhler equation.

Water solubilities for adipic and succinic acid reported in the literature (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Raymond and Pandis, 2002) vary around the values of 25 g l^{-1} for adipic acid and 88 g l^{-1} for succinic acid reported by Saxena and Hildemann (1996). In this work we use the values reported by Saxena and Hildemann (1996). For the purpose of this work water activity coefficients of unity and surface tensions equal to that of pure water were used in all calculations.

Figures 1a and b show plots of supersaturation versus wet particle diameter for adipic and succinic acid, respectively, with varying amounts of NaCl calculated using eq. (1) ($\nu_{\mathrm{NaCl}} = 2$, $\nu_{\mathrm{adipic}} = 1$, $\nu_{\mathrm{succinic}} = 1$). Particles that are exposed to the maximum supersaturation (critical supersaturation) are said to activate and start to grow limited only by diffusion of water molecules to the surface.

It is illustrated in Fig. 1 that the modified Köhler equation predicts two maxima for supersaturation as a function of droplet diameter and there is a cusp at the minimum droplet diameter where all organic material is dissolved. The first maximum (SSc_1) is found before all slightly soluble material is dissolved and the second maximum (SSc_2) is located after. In the following we refer to these two parts of the modified Köhler curve

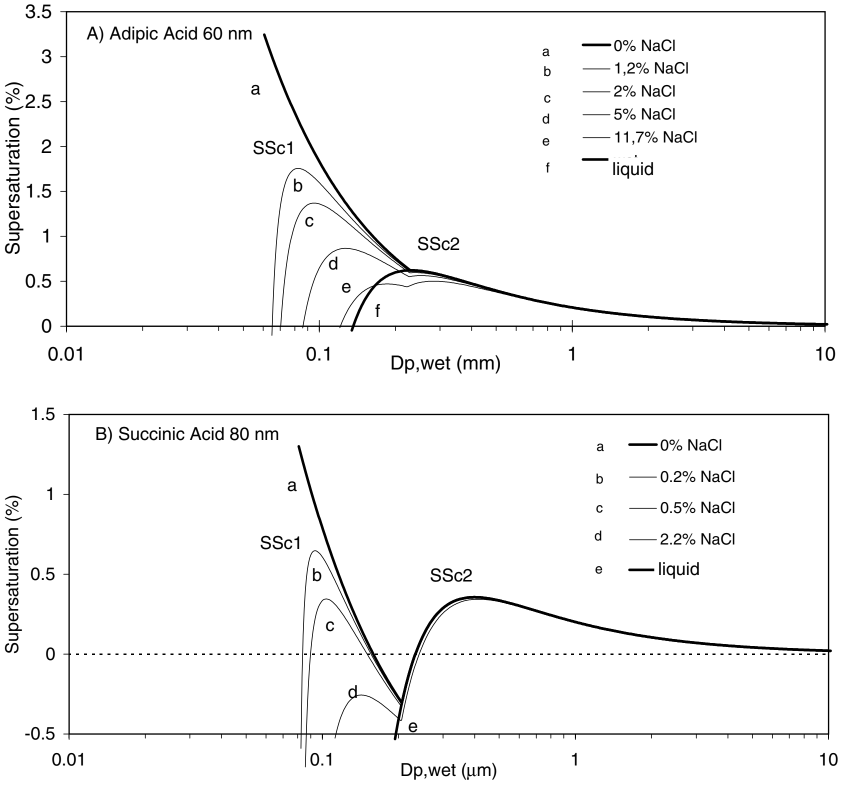

Fig 1. Köhler curves modified to take account of limited solubility for (a) adipic acid particles (60-nm dry diameter) and (b) succinic acid particles (80-nm dry diameter) with varying amounts of NaCl at 298 K.

as the SSc_1-dominated regime and the SSc_2-dominated regime, respectively. As seen from Fig. 1 SSc_1 constitutes a strong activation barrier that decreases significantly when a small amount of inorganic salt is present. SSc_2 is also affected by the presence of salt but less dramatically than SSc_1.

We note that a particle needs an undissolved core to be in the SSc_1-dominated regime. If a particle is a supersaturated solution of organic molecules we expect that the activation barrier constituted by SSc_1 is eliminated and that the particle activates according to traditional Köhler theory as though the organic acid was infinitely soluble. This is also illustrated in Fig. 1 (denoted liquid).

This work focus on two aspects of cloud droplet activation of slightly soluble organics: (1) the effect of small amounts of salt on critical supersaturation and (2) the difference in expected behaviour of particles containing a solid organic core and particles that are supersaturated solutions of organic material.

3. Experimental

In the first series of experiments a monodisperse aerosol was generated by atomizing aqueous solutions of organic compounds and salt. Particles were dried in diffusion dryers followed by dilution with dry clean air to relative humidities in the range 2–20%. From our observation (Bilde et al. 2003) that vapor pressures of C3–C9 dicarboxylic acid particles dried in this way show an odd–even alternation that can be related to solid-state structure we feel confident that our particles are different from liquid particles and we will refer to them as solid.

Particles were charged by exposing them to a Kr-85 bipolar ion source. A monodisperse aerosol obtained using a differential mobility analyzer (DMA, TSI, 3080) was divided between a condensation particle counter (TSI, 3010) and a static thermal-gradient diffusion cloud condensation nucleus chamber, model CCNC-100B from the University of Wyoming, Department of Atmospheric Science (Snider and Brenguier, 2000; Delene and Deshler, 2000; Snider et al. 2003). The CCNC-100B was calibrated using monodisperse NaCl and $(NH_4)_2SO_4$ particles. Experimental supersaturations are obtained from the temperature difference between top and bottom plates in the CCN chamber. Theoretical values are obtained using traditional Köhler theory. Van't Hoff factors as a function of particle size were calculated from data by Low, (1969) for $(NH_4)_2SO_4$. A van't Hoff factor of 2 was used for all sizes of NaCl particles. No shape factors were applied. Figure 2 shows that there is a linear relationship between theoretical and experimental values of critical supersaturation for NaCl and $(NH_4)_2SO_4$ particles over the supersaturation range 0.2–1.8%. All supersaturations reported in this work were corrected according to this linear relationship.

We first noticed that particles made by atomizing a solution of succinic acid in double de-ionized water activated almost as though they were infinitely soluble, whereas particles made by atomizing the acid dissolved in double de-ionized water purified in our Milli-Q PLUS Ultra Pure Water System showed less tendency to activate (a plot of the fraction of activated particles versus supersaturation showed a very broad range of supersaturations for activation and in some cases 100% activation was not reached below 2% supersaturation). This was a strong indication that trace amounts of impurity facilitate the cloud droplet activation of pure organic particles and motivated us to elaborate on the amount of salt in the particle. Commercial water (Fluka, 17749) purified by reverse osmosis, ion-exchange treatment and

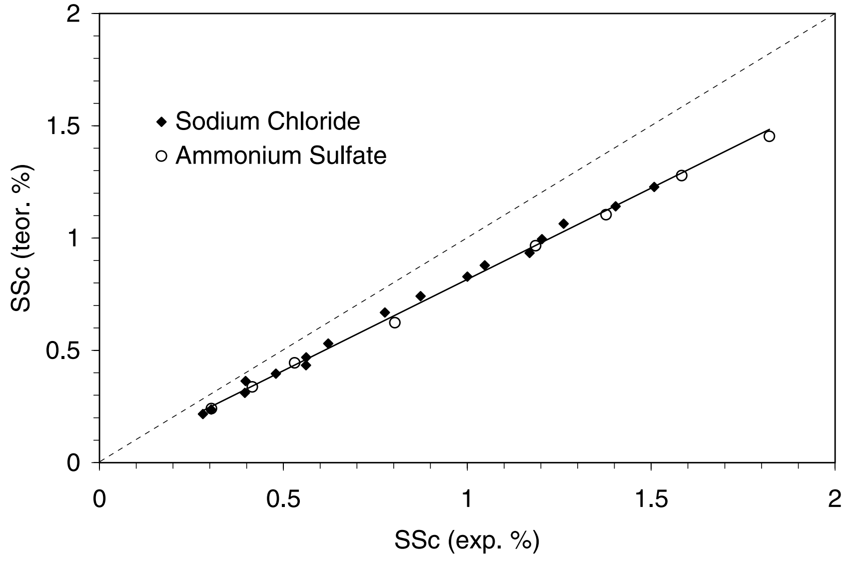

Fig 2. Calibration curve for the cloud condensation nucleus chamber. Theoretical versus experimental critical supersaturations for NaCl and $(NH_4)_2SO_4$ particles.

microfiltration (in the following referred to as ultrapure water) produced a similar or smaller mass per volume of residual particles (when atomized alone) compared with our Mili-Q water and was used throughout the rest of this work. Other precautions to avoid impurities included cleaning glassware in water only and thorough flushing of the atomizer with Milli-Q water followed by ultra-pure water before each experiment. Purity of the organic acids used were 99.8% for adipic acid (Riedel-de-Han AG) and ≥99.5% for succinic acid (MERCK KGaA).

4. Importance of small amounts of inorganic salt

Figure 3a shows the fraction of activated particles versus supersaturation for 60-nm pure adipic acid particles and particles with 1.2%, 2%, 5% and 11.7% (wt) NaCl, respectively. Notice that the pure adipic acid particles do not activate at supersaturations below 2%. Increasing amounts of NaCl dramatically increase the tendency to activate until a certain threshold value of NaCl after which the effect is more moderate. This suggests that SSc_1 is determining the critical supersaturation before the threshold value, and SSc_2 is dominating thereafter. Similar curves were obtained for dry particle diameters of 80, 100 and 120 nm. For larger particles, less NaCl is needed for SSc_1 to be smaller than SSc_2.

Two steps in the activation curves are observed. The DMA selects particles based on electrical mobility and a fraction of the exiting particles is multiply charged. The first step at low supersaturation is consistent with activation of doubly charged (and thus larger) particles. Doubly charged particles can also explain the observation that one-fifth of the particles are activated at 2% supersaturation when no NaCl is added. Based on the modified Köhler equation a steep rise in a plot of CCN/CN versus supersaturation at either SSc_1 or SSc_2 is expected for all concentrations of NaCl used. We ascribe the broad range of supersaturations for activation seen for some of the experiments in Fig. 3 to the very large sensitivity to small amounts of impurity when $SSc_1 > SSc_2$ and our inability to make a perfect internal aerosol mixture.

Figure 3b shows experimental results for succinic acid particles with varying amounts of salt. Owing to the higher water solubility of succinic acid compared with adipic acid SSc_1 is significantly lower and the sensitivity to small amounts of salt even more pronounced than for adipic acid. As a consequence we are not able to avoid the effect of trace amounts of impurities and as illustrated in Fig. 3b we observe a broad onset of activation for dry (solid) 80-nm particles of succinic acid. Notice also that addition of as little as 0.5% of NaCl changes the critical supersaturation significantly (from ~0.8% to ~0.38%). Further increase of the amount of NaCl to 2.2% made no additional change in

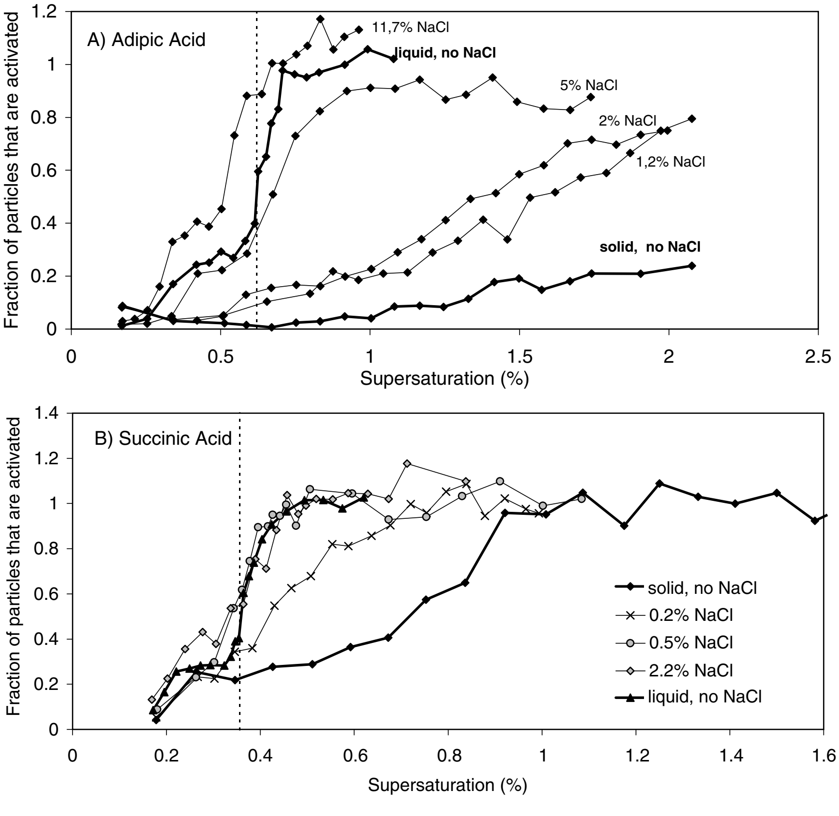

Fig 3. Fraction of activated particles as a function of supersaturation for (a) 60-nm (dry size) adipic acid particles and (b) 80-nm (dry size) succinic acid particles with varying amounts of NaCl. The data labeled "liquid, no NaCl" represent the particles that were introduced into the cloud condensation nucleus chamber as supersaturated solution droplets. Each point represents the average of several measurements. The dotted lines represent critical supersaturations (SSc2) predicted from traditional Köhler theory.

critical supersaturation. The critical supersaturation observed when 0.5% and 2.2%, respectively of NaCl are added to the particles is consistent with the location of SSc_2 and we interpret the shift in critical supersaturation as reflecting a transition from the SSc_1 to the SSc_2-dominated regime. Similar results were found for 60 and 100 nm particles. For a dry particle diameter of 120 nm SSc_1 and SSc_2 are equal when as little as 0.03 wt% NaCl equivalent is present. Such small impurities are unavoidable in our experiments and consistently we found that 120 nm (dry size) particles of succinic acid activate at supersaturations close to 0.2% (SSc_2).

As mentioned in the introduction previous studies of adipic and succinic acid: Cruz and Pandis (1997), Corrigan and Novakov (1999), Prenni et al. (2001), Raymond and Pandis (2002), have shown discrepancies between experimental results and theory in the form of the modified Köhler equation: pure succinic acid, $HOOC(CH_2)_2COOH$, apparently activated according to traditional Köhler theory as though it was infinitely soluble even though modified Köhler theory predicts a higher critical supersaturation and adipic acid, $HOOC(CH_2)_4COOH$, apparently obeyed neither traditional nor modified Köhler theory and different results were obtained in different experiments. The behavior of succinic acid, the discrepancies between literature data for activation of adipic acid particles: the breakdown of traditional Köhler theory, the broad onset of activation and the large variability described in the literature may now be explained by modified Köhler theory and the large effect of small amounts of impurities equivalent to a few wt% (or less) NaCl. It is not unreasonable that impurities of this size are present in the water and/or the commercial samples of adipic and succinic acid.

Figures 4a and b show observed and calculated critical supersaturations for adipic acid versus mass fraction of NaCl in the particle for 80- and 120-nm particles (dry size), respectively. The adipic acid used may contain up to 0.2% unspecified impurities and we cannot completely avoid impurities in the water. Particles with no NaCl added are therefore assumed to contain impurities equivalent to 0.2 ± 0.2 wt% NaCl. The solid lines shows calculated values of the maximum of SSc1 and SSc2 from Köhler theory modified to take account of limited solubility. SSc1 is dominating to the left of the critical point and SSc2 is dominating to the right as also indicated in Fig. 4. Observed and calculated critical supersaturations agree well and our experimental results are consistent with Köhler theory modified to account for limited solubility. The transition from the SSc_1-dominated regime to the SSc_2-dominated regime as more NaCl is added to the particle is clearly seen in Fig. 4.

As mentioned in the introduction we used the surface tension of pure water in all calculations. Surface tensions of pure adipic and succinic acid solutions have however been measured by Shulman et al. (1996) and appear to differ by 10% or less from the surface tension of pure water at saturation. A decrease in surface tension of 10% reduces SSc1 by <15% for an 80-nm dry pure particle of adipic acid. To the best of our knowledge no data on surface tensions for mixtures of either succinic nor adipic acid and NaCl exist. Sensitivity analysis for the solubility of adipic acid shows that a 25% decrease (or increase) in the solubility used for calculations (25 g l^{-1} from Saxena and Hildemann, 1996) results in an increase (decrease) of SSc1 of <5% for an 80-nm dry particle. Succinic acid is more sensitive to errors in the used surface tension and solubility than adipic acid. Even so, this is not significant for our conclusion that small amounts of salt have a large effect on critical supersaturation.

Most atmospheric particles are considered to be mixtures of organic and inorganic compounds. For the majority of these particles, compounds with solubilities similar to those of adipic and succinic acid can be treated as infinitely soluble when calculating critical supersaturations. However, there can be aerosol particles that contain such small amounts of inorganic ions or other very water-soluble compounds that the solubility becomes limiting for activation. Hygroscopic TDMA measurements on atmospheric aerosols show one group of particles with a growth factor distribution that approaches 1, indicating that particles with a few per cent, or less, of inorganic ions exist in the atmosphere (see, for example, Svenningsson et al. 1994; Swietlicki et al. 1999). The ability of these particles to activate to cloud droplets determines whether they deposit via precipitation. Knowledge about how much soluble material they need to accumulate for SSc2 to be dominant is therefore important for evaluating, for example, particle lifetimes in the atmosphere.

Interestingly, a large effect of small amounts of salt on the cloud droplet activation of leucine was recently observed by Raymond and Pandis (2003), who also conclude that this may have important implications for modelling the activation of mixed particles in the atmosphere.

5. Particle phase and humidity history

We now proceed to the hypothesis that a particle needs an undissolved core to be in the SSc_1-dominated regime and that the activation barrier constituted by SSc_1 is eliminated if the particle is a supersaturated solution of an organic compound. To test this hypothesis organic acid particles that were supersaturated aqueous solutions of adipic acid were introduced into the cloud condensation nucleus chamber. Such solution droplets were created by bypassing the diffusion dryers and leading the particles directly from the atomizer over the Kr-85 source and into the DMA. The recirculating sheath air in the DMA was kept at a relative humidity of 82 ± 1%. The exiting wet monodisperse aerosol was divided into two: one part entered the CCNC and the other part was dried to a relative humidity well below 20% by dilution with dry clean air. Crystallization relative humidity is ∼56% for succinic acid and ∼30% for glutaric acid (Peng et al. 2001). Water solubility of dicarboxylic acids alternates with the parity of the number of carbon atoms and glutaric acid is more water soluble than both succinic and adipic acid (Saxena

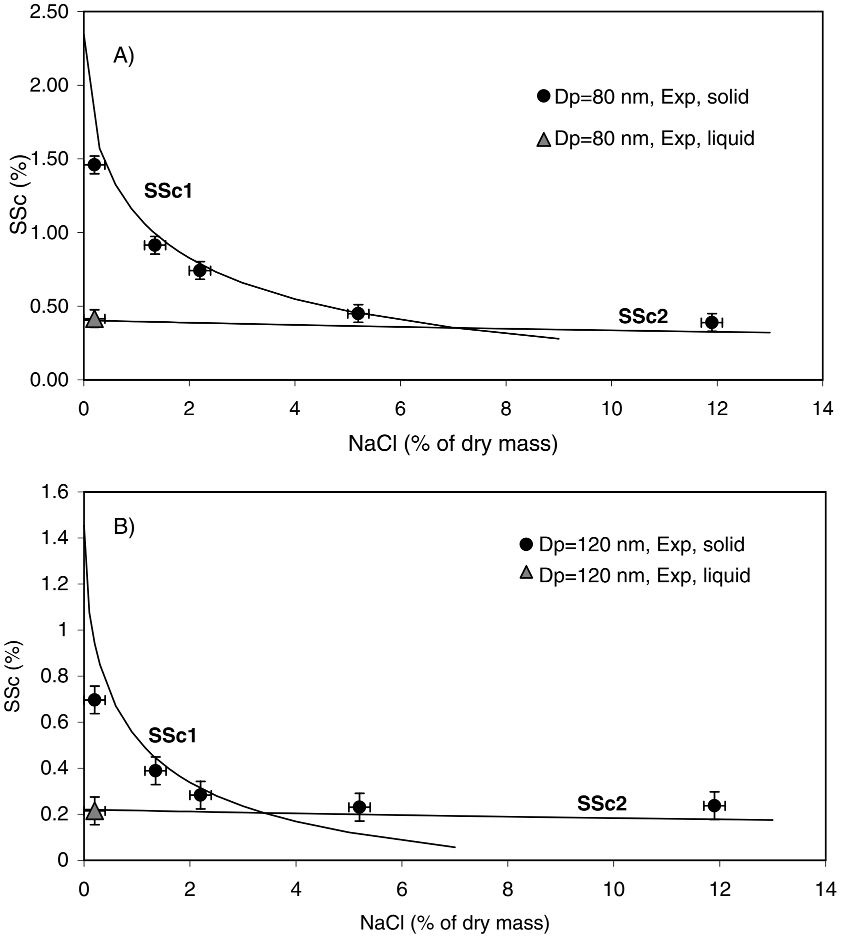

Fig 4. Observed critical supersaturations versus chemical composition for mixed particles of adipic acid and NaCl. (a) Dry size of 80 nm and (b) dry size of 120 nm. Lines represent calculated values of critical supersaturation. There is a critical point where $SSc_1 = SSc_2$. To the left of this point critical supersaturation is determined by SSc_1 and to the right of this point critical supersaturation is determined by SSc_2. Circles represent activation of initially dry particles. Triangles represent particles that are supersaturated solutions of organic material. Errorbars reflects a 0.2% uncertainty in particle composition and estimated uncertainty on the critical supersaturation (three standard deviations obtained from linear least squares analysis of the calibration data in Fig. 2).

and Hildemann, 1996; Shulman et al. 1996). Both succinic and adipic acid particles should thus be dry at relative humidities below 20%. The size of the dry aerosol particles were measured with an SMPS (TSI 3934) system. Comparison of residence times in the system and evaporation rates of adipic and succinic acids reported by Tao and McMurry (1989) and Bilde et al. (2003) showed that evaporation of the dry particles can be neglected. In agreement with our predictions pure particles of adipic acid (with dry sizes corresponding to diameters of 60, 80, 100 and 120 nm, respectively) activated at SSc_2 when they were introduced into the cloud condensation nucleus chamber as supersaturated solutions (in the following referred to as liquid particles). The diameters of the liquid particles introduced into the cloud chamber were always well below the critical diameters (SSc_2) corresponding to their dry size. For illustration the activation of liquid particles are shown in Fig. 3 (bold lines) and in Fig. 4 as triangles. Similar experiments were performed on succinic acid with similar results. When liquid particles of succinic acid (corresponding to dry diameters of 60, 80, 100 and 120 nm, respectively) were introduced into the cloud chamber activation was observed at supersaturations corresponding to SSc2.

If not formed in the liquid state a pure particle of adipic acid or similar slightly soluble compound in the atmosphere must go through a cloud cycle to become liquid and exist as a supersaturated solution droplet. During this process it will most likely collect inorganic material and become a multicomponent solution droplet. Multicomponent liquid particles where the slightly soluble component exists as a supersaturated solution may therefore be even more relevant for the atmosphere than the pure liquid particles studied herein. Such multicomponent liquid particles will be investigated in a future study.

6. Conclusions

We show that small amounts of salt may have a dramatic effect on critical supersaturation of slightly soluble organic compounds and we have experimentally confirmed the two maxima predicted by Köhler theory modified to account for limited solubility. Our results can explain the apparent gap between experimental data and theory in the form of the modified Köhler equation for succinic and adipic acid in previous studies.

In summary, if a particle contains an undissolved core of organic material there is a barrier to water uptake and activation, which is decreased by the presence of inorganic salt. Activation may therefore be limited by either SSc_1 or SSc_2. We suggest that the barrier to activation is eliminated when the particle is a supersaturated solution of slightly soluble organic material and activation is determined by SSc_2 only. We confirm this experimentally for adipic and succinic acid.

This work implies that small amounts of salt and particle phase are important parameters for modelling of the aerosol indirect effect and interpretation of experimental data on CCN activity. Cloud processing during which an organic particle collects inorganic material and/or changes phase may have a dramatic effect on the ability of the particle to act as cloud condensation nuclei.

7. Acknowledgments

We gratefully acknowledge the Danish Natural Science Research Council for funding this work. We thank the Department of Atmospheric Science, University of Wyoming, for building the CCNC and sharing their expertise on the instrument with us. We thank Thomas Rosenorn and Jacob Monster for assistance in calibrating the CCNC.

References

Bilde, M., Svenningsson, B., Monster, J. and Rosenorn, T. 2003. Even–odd alternation of evaporation rates and vapor pressures of C3–C9 dicarboxylic acids. *Environ. Sci. Technol.* **37**, 1371–1378.

Corrigan, C. E. and Novakov, T. 1999. Cloud condensation nucleus activity of organic compounds: a laboratory study. *Atmos. Environ.* **33**, 2661–2668.

Cruz, C. N. and Pandis, S. N. 1997. A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei. *Atmos. Environ.* **15**, 2205–2214.

Delene, J. D. and Deshler, T. 2000. Calibration of a photometric cloud condensation nucleus counter designed for deployment on a balloon package. *J. Atmos. Ocean. Tech.* **17**, 459–467.

IPCC, 2001. Climate Change 2001: the scientific basis. In: *Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge.

Köhler, H. 1936. The nucleus in the growth of hygroscopic droplets. *Trans. Faraday. Soc.* **32**, 1152–1161.

Kulmala, M., Laaksonen, A., Charlson, R. J. and Korhonen, P. 1997. Clouds without supersaturation. *Nature* **388**, 336–337.

Laaksonen, A., Korhonen, P., Kulmala, M. and Charlson, R. J. 1998. Modification of the Köhler equation to include soluble trace gases and slightly soluble substances. *J. Atmos. Sci.* **55**, 853–862.

Low, R. D. H. 1969. A theoretical study of nineteen condensation nuclei. *J. Rech. Atmos.* **4**, 65–78.

Peng, C., Chan, M. N. and Chan, C. K. 2001. The hygroscopic properties of dicarboxylic and multifunctional acids: measurements and UNIFAC predictions. *Environ. Sci. Technol.* **35**, 4495–4501.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E. Russel, L. M. and Ming, Y. 2001. The effects of low molecular weight dicarboxylic acids on cloud formation. *J. Phys. Chem. A* **105**, 11 240–11 248.

Raymond, T. M. and Pandis, S. N. 2002. Cloud activation of single-component organic aerosol particles. *J. Geophys. Res.* **107**, doi : 10.1029/2002JD002159.

Raymond, T. R. and Pandis, S. N. 2003. Formation of cloud droplets by multi-component organic aerosol particles. *J. Geophys. Res.* **108**, doi : 10.1029/2003JD003503.

Saxena, P. and Hildemann, L. M. 1996. Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds. *J. Atmos. Chem.* **24**, 57–509.

Shulman, M. L., Jacobson, M. C., Charlson, R. J., Synovec, R. E. and Young, T. E. 1996. Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets. *Geophys. Res. Lett.* **23**, 277–280.

Snider, J. R. and Brenguier, J. L. 2000. Cloud condensation nuclei and cloud droplet measurements during ACE-2. *Tellus* **52B**, 828–842.

Snider, J. R., Guibert, S., Brenguier, J.-L. and Putaud, J.-P. 2003. Aerosol activation in marine stratocumulus clouds Part-II: Köhler and Parcel theory closure studies. *J. Geophys. Res.* **108**, 8629, doi : 10.1029/2002JD002692.

Svenningsson, B., Hansson, H.-C., Wiedensohler, A., Noone, K., Ogren, J., Hallberg, A. and Colvile, R. 1994. Hygroscopic growth of aerosol particles and its influence on nucleation scavenging in cloud: experimental results from Kleiner Feldberg. *J. Atmos. Chem.* **19**, 129–152.

Swietlicki, E., Zhou, J., Berg, O. H., Martinsson, B. G., Frank, G., Cederfelt, S., Dusek, U., Berner, A., Birmili, W., Wiedensohler, A., Yuskiewicz, B. and Bower, K. N. 1999. A closure study of submicrometer aerosol particle hygroscopic behaviour. *Atm. Res.* **50**, 205–240.

Tao, Y. and McMurry, P. H. 1989. Vapor pressures and surface free energies of C14–C18 monocarboxylic acids and C5 and C6 dicarboxylic acids. *Environ. Sci. Technol.* **23**, 1519–1523.