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Cloud Droplet Activation of Amino Acid Aerosol Particles

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In this work we investigated the ability of a series of amino acids to act as cloud condensation nuclei using a static thermal gradient diffusion type cloud condensation nucleus counter. Particles of pure dry L-glycine, glycyl-glycine, L-serine, L-methionine, L-glutamic acid, L-aspartic acid, and L-tyrosine were studied as well as internally mixed dry particles containing ammonium sulfate and one or two of the following amino acids: L-methionine, L-aspartic acid, or L-tyrosine. The amino acids ranged in water solubility from high (>100 g/L), intermediate (10−100 g/L), low (3−10 g/L), to very low (<3 g/L). With the exception of L-methionine and L-tyrosine, all the studied pure amino acid particles activated as though they were fully soluble, although Köhler theory modified to account for limited solubility suggests that the activation of the intermediate and low solubility amino acids L-serine, L-glutamic acid, and L-aspartic acid should be limited by solubility. Activation of mixed particles containing at least 60% dry mass of L-tyrosine was limited by solubility, but the activation of the other investigated mixed particles behaved as if fully soluble. In general, the results show that particles containing amino acids at atmospherically relevant mixture ratios are good cloud condensation nuclei.

1. Introduction

Aerosol particles in the troposphere influence the climate of the earth, both directly and indirectly, by a number of mechanisms. One of the major uncertainties in the current understanding of the climate system is the effect that particles have on cloud processes and the resulting effect on the radiation balance.[1]

The ability of a particle to activate and act as a cloud condensation nuclei (CCN) and subsequently become a cloud droplet depends partly on the chemical composition and partly on the physical properties of the particles. The supersaturation at which a particle can activate is termed the critical supersaturation (*Sc*) and only a fraction of all particles is capable of activating under atmospheric conditions.

Atmospheric aerosol particles normally contain thousands of different organic compounds, elemental carbon, and inorganic compounds, each affecting the CCN capacity in different ways. Several types of these compounds and their CCN activity as function of size and supersaturation have recently been investigated in detail and reviewed by Sun and Ariya.[2]

The present work seeks to expand the current knowledge base and the number of investigated compounds by investigating a number of species that are commonly found in the water-soluble organic nitrogen (WSON) fraction of atmospheric particles, namely amino acids.

Normally, three amino acid fractions can be analyzed in aerosol samples, and these are the following: (1) DCAA: dissolved combined amino acids, i.e. proteins and peptides;[3] (2) DFAA: dissolved free amino acids, from the hydrolysis of DCAA;[4−6] and (3) PAA: particulate amino acids, which are micrometer-sized solid microorganisms and debris particles found inside the liquid phase of aerosol particles.[3]

Bubble bursting and jet drop production in the oceans produce sea spray particles containing amino acids originating from phytoplankton (L-isomer amino acids) and from bacteria (D-isomer amino acids).[3] The phytoplankton matter in sea spray dominates in coastal-near areas,[3] while the bacterial content seems to make a significant contribution in off-shore marine aerosol particles.[7,8] Continental sources also contribute to the marine particle phase amino acids. Whether continental particles or sea spray particles are the major source of remote oceanic particle amino acids is disputed. Wedyan and Preston[8] and Mace et al.[9] argue based on a back trajectory analysis that particle phase amino acids from remote marine areas should be mainly of sea spray origin. Matsumoto and Uematsu[10] on the other hand infer from trajectories and source tracers that the fine mode (<2.5 μm diameter) aerosol particle DFAA is dominated by a continental origin even at remote oceanic locations, while the coarse DFAA fraction should mainly be of phytoplankton sea spray origin. However, in the above studies it is concluded that neither source can be ruled out as an important contributor to total particle mass or the fine and coarse fraction.

The different types of amino acids in continental particles are thought to come from plant debris, pollen, and algae,[11] as well as yeast and fungi and bacteria spores.[4,12] The source contributions of these continental amino acids are, however, far from being properly characterized. Mace et al.[9] indicate an anthropogenic coarse mode (>1 μm diameter) protein processed soil DFAA source and a fine mode bioaerosol source from Tasmania in their particles, and Mace et al.[13] show that both biomass burning as well as natural Amazon forest environments contain dissolved free amino acids in the particle phase. The data analysis by Zhang et al.[14] suggests that DCAA and DFAA PM2.5 compounds come from background sources. Mader et

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al.[15] show a preference of DCAA and DFAA compounds in pollution outbreaks from inland China with dust outbreaks as the second place producer of amino acids. Moreover, Zhang and Anastasio[11] imply livestock farming as a major source of bacterially produced ornithine in the DFAA and DCAA PM2.5 fraction over California. Mace et al.[12] suggest fungi and bacteria spores from Saharan dust and possibly long-range transport as an important source of Mediterranean DFAA. Finally, Tarr et al.[16] show that sunlight irradiated fulvic acid could be an important source of DFAA. Hence, a variety of sources could produce amino acids in the particle phase, although soil and desert dust seem to be the most frequent explanation of high concentrations of amino acids. Neither study gives an explanation of how amino compounds are transferred to the PM2.5 fraction in the first place.

The amino acid compounds found in aerosol samples of mainly marine character are predominantly alanine, arganine, glycine, leucine, phenylalanine, proline, serine, and valine,[8,9] and for aerosols of mainly continental origin they are alanine, arganine, glycine, histine, lysine, ornithine, proline, serine, threonine, tyrosine, and valine.[11−13,15] However, there are several other amino acids that are found in significant concentrations in both environments.

Concentration ranges for aerosol amino acids with a marine character are 0.3−1094 pmol of nitrogen DFAA per cubic meter of air (pmol N m^{-3}).[9,17] Wedyan and Preston[8] give a range of 130−2000 pmol of total organic mass of DFAA + DCAA + PAA m^{-3} for what they argue are sea spray dominated aerosols, while Matsumoto and Ueamatsu[10] and Mace et al.[9] results fit inside the range 1.5−220 pmol N m^{-3} for what they believe is DFAA coming from a mixed influence of continental and marine sources. For aerosols with a continental preference we have concentrations of 20−1120 pmol DFAA N m^{-3},[12,13] 510−2850 pmol DFAA + DCAA m^{-3},[15] and 1470−4930 pmol DFAA + DCAA + alkyl amines N m^{-3}.[14]

The DFAA nitrogen values comprise 1−17% of total water-soluble organic nitrogen (WSON) in the aerosol particles in different environments.[9,12,17] DFAA + DCAA carbon comprises 1.5−4% of total water-soluble organic carbon (WSOC) from polluted China,[15] and Zhang et al.[14] show that the DFAA + DCAA including alkyl amines nitrogen comprises a median 23% of WSON in California.

The work referenced above shows that the characterization of sources of amino acids in atmospheric aerosols remains in its infancy, that it is highly speculative in some areas, and that more work is needed to be able to create an adequate global amino acids aerosol particle budget. Many of these studies include only measurements of the DFAA fraction, thereby missing the sources of DCAA and PAA. The DCAA concentration is on average on the order of 5 to 10 times higher than that of DFAA in both continental and sea spray aerosol samples[3,8,11,14] and it precedes the DFAA formation through hydrolysis in the liquid phase. Furthermore, the PAA concentration is once reported to be ∼3 times higher than the DFAA + DCAA concentration.[8]

The focus of this study is the cloud droplet activation of particles containing amino acids. We studied mixed particles containing one amino acid (L-aspartic acid, L-methionine, or L-tyrosine) and ammonium sulfate or two amino acids (L-aspartic acid and L-tyrosine) and ammonium sulfate. For completeness we also investigated dry single component particles containing L-glycine, glycyl-glycine, L-serine, L-methionine, L-glutamic acid, L-aspartic acid, or L-tyrosine. These amino acids were selected based on their atmospheric relevance and their broad spectrum of water solubilities.

The results are compared to two previous references covering the CCN activation of L-aspartic acid and L-glutamic acid. We investigate whether the activation behavior can be predicted using Köhler theory assuming either limited or full solubility and discuss our results in a general framework with respect to the importance of water solubility of organic aerosol constituents and cloud droplet activation.

2. Theoretical Basis

Köhler theory[18] describes how two opposing effects determine the vapor pressure of water over a solution droplet, namely the Kelvin effect, which is the elevation of vapor pressure due to the curvature of the droplet, and the Raoult effect, which is the reduction in vapor pressure due to the change in water activity with the presence of a solute. In the following we use the same notation and theoretical framework as in Bilde and Svenningsson[19] and Rosenørn et al.[20]

The saturation ratio, s, of water over an aqueous solution droplet is given by the Köhler equation formulated as the product of the water activity and the Kelvin effect:

$$s \equiv \frac{p}{p_0} = a_w \exp\left(\frac{4M_w\sigma}{RT\rho D_p}\right) \quad (1)$$

where p is the vapor pressure of water over a droplet, p_0 is the water vapor pressure over a flat surface of pure water, a_w is the water activity of the solution, M_w is the molar mass of water, σ is the liquid−air surface tension, R is the gas constant, T is the temperature, ρ is the density of the solution, and D_p is the droplet diameter. The experiments in this study were performed at 295.15 K and the values for surface tension and the density of the solution have been approximated by the values for pure water (0.0724 J m^{-2} (ref 21) and 997.8 kg m^{-3} (ref 22), respectively).

The supersaturation ss is defined as $s - 1$. The critical supersaturation (Sc) is the maximum on a plot of ss versus D_p (the Köhler curve) where the particle undergoes cloud droplet activation and the particle starts to grow in size only limited by diffusion of water to the droplet.

The water activity in this work is calculated by using van't Hoff factors (i):

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

where the subscripts i and w denote solute and water and n_i is the number of moles of compound i. For the amino acids van't Hoff factors of 1 were used. For ammonium sulfate a concentration-dependent van't Hoff factor was used as explained in Section 3.

We assume that the particles are initially solid. If the particle dissolves completely during activation, the number of moles of compound i can be calculated as $\pi\beta_i\rho d_0^3/6M_i$, where d_0 is the dry particle diameter, β_i is the mass fraction of species i, and ρ is the density of the particle. The particle is said to activate according to Köhler theory assuming full solubility. However, if a solid core is maintained during activation, the Köhler curve has a second maximum and the activation is said to be limited by solubility. To account for limited solubility, the number of moles of species i, n_i, is expressed as the minimum value of the two terms in

$$n_i = \min\left[\frac{\beta_i \rho d_0^3}{M_i}, \frac{(D_p^3 - d_0^3)C_{sat}}{M_i}\right]\frac{\pi}{6} \quad (3)$$

where D_p is the droplet diameter and C_{sat} is the solubility; the particle density is calculated as

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

assuming additivity of volumes in the particle. The water solubility and density values of ammonium sulfate used in this work are 764 kg m^{-3} and 1770 kg m^{-3}, respectively.

3. Experimental Section

Critical supersaturation values were measured with a condensation nucleus counter (Wyoming CCNC 100B) in an experimental setup that has been described in previous papers.[19,20,23] Particles were generated by atomizing a solution of the compound of interest dissolved in 18.2 MΩ Milli-Q water, using a TSI constant output atomizer (TSI-3076) running on purified air. The aerosol was dried by passing it through two diffusion driers before entering a Kr-85 bipolar ion source (TSI 3077 aerosol neutralizer) to obtain particles of a known charge distribution. The aerosol was then further dried by dilution with purified air to a final relative humidity of ≤6%. Using a differential mobility analyzer (TSI DMA model 3081) (sheath to aerosol flow ratio of ~10:1), a narrow size distribution was selected for analysis. The resulting aerosol was divided between the cloud condensation nucleus counter and a condensation particle counter (TSI CPC model 3010). As a check, the CPC was periodically replaced by an SMPS system (TSI SMPS model 3934) to ensure that the sizing of the first DMA was correct and that no significant evaporation of the particles took place in the experimental setup. No discrepancy in the size distribution was observed between the DMA and the SMPS system in the course of these experiments. All experiments were performed at around 295 K and the particle concentration was in the range 200−1000 cm^{-3}.

The Wyoming CCNC 100B is a static thermal gradient diffusion type counter and has previously been described in detail.[24−27] The supersaturation profile in the chamber was calculated assuming linear gradients of water vapor partial pressure and temperature in the chamber.[28] The supersaturation in the chamber was calibrated by using NaCl and $(NH_4)_2SO_4$ particles as explained in Bilde and Svenningsson.[19] A van't Hoff factor of 2 and no shape factor was used for sodium chloride. For ammonium sulfate a concentration-dependent van't Hoff factor was used as explained by model "VH1" in the paper by Rose et al.[29] No shape factor was used. The experiments during this study were performed during four intensive measurement periods distributed over several years, and the chamber supersaturation was calibrated in each period. Amino acids were obtained from commercial sources and used as received, see Table 1. Ammonium sulfate was obtained from Sigma Aldrich with a purity of 99.999%.

During the actual measurements, a spectrum of the fraction of activated particles, namely the number of activated cloud droplets measured by the CCNC divided by the total number of particles measured by the CPC as a function of supersaturation, was obtained (cf. Figure 1 for a typical activation spectrum). Ideally, the activation spectrum from the CCNC to a monodisperse aerosol would be a step function. However, the aerosol exiting the DMA is not completely monodisperse. By taking only the width of the transfer function of the DMA into account,[43] it was in most cases possible to fit the slope of the response curve (solid line in Figure 1). The critical supersaturation is defined as the supersaturation on the fitted line where the activated fraction is lying halfway between the fitted plateaus ($Sc = 1.01\%$ for the example in Figure 1). There are other ways to fit the data. It is possible to use, for example a fit that does not take the transfer function into account, such as the error function method described in Snider et al.[44] For the current data set both methods fitted the data well.

4. Results and Discussion

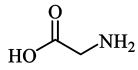
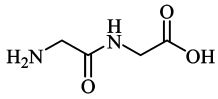
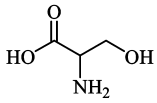
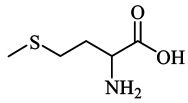
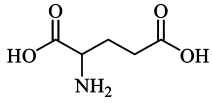
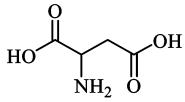
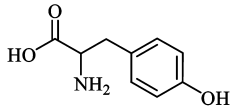
4.1. Single Component Particles. Figure 2 shows measured critical supersaturations (*Sc*) versus dry particle diameters for five of the seven investigated amino compounds. The error bars for the experimental data in Figure 2 represent two standard deviations of the mean of the four sets of supersaturation calibrations, and are dependent on the absolute value of the supersaturation. The same type of error ranges are also shown in Figures 3−6. The calculated Köhler curves accounting for limited solubility and assuming full solubility are also shown in Figure 2. The graphs demonstrate that the effect of limited solubility is largest for small particle sizes.

Inspired by Huff-Hartz et al.[42] we divide the amino acids into four solubility classes: high solubility (>100 g L^{-1}), intermediate solubility (10−100 g L^{-1}), low solubility (3−10 g L^{-1}), and very low solubility (<3 g L^{-1}). From Figure 2 it can be seen that the two highly soluble compounds L-glycine and glycyl-glycine activate at supersaturations slightly higher than predicted by Köhler theory. In the following we discuss possible reasons for this slight underprediction by the Köhler model. First, we can exclude that limited solubility is playing a role since Köhler theory shows that solubility is not a limiting factor for the critical supersaturation for the investigated sizes (50−150 nm diameter and 60−150 nm diameter for L-glycine and glycyl-glycine, respectively). Unfortunately, we were not able to obtain reliable data for 50 nm diameter glycyl-glycine particles.

Another issue could be surface tension. Some amino acids can behave as inorganic salts and increase surface tension in aqueous solution compared to pure water while other amino acids can lower the surface tension.[45] Experimental data on the surface tension of L-glycine in aqueous solution are available from Matubayasi et al.[46] This study shows that the increase in surface tension of the L-glycine solution compared to pure water at the concentration at activation (<0.3 mol/kg for the particle sizes studied herein) is less than 1%. This results in an increase of predicted critical supersaturation from 0.763% to 0.775% for a 40 nm diameter particle. This brings our predicted values closer to the experimental, although the change is almost negligible. Since the surfactant strength for these compounds is very low at the concentrations relevant for cloud droplet activation, partitioning between the droplet bulk and surface as described by Sorjamaa et al.,[47] Li et al.,[48] and Prisle et al.[49] is considered insignificant for the purpose of these calculations.

Nonideality is another issue to consider. We have assumed the water activity coefficients to be unity in all cases, expressed by van't Hoff factors of 1. If the van't Hoff factors of L-glycine and glycyl-glycine are roughly 0.87, the calculated critical supersaturation and the measured critical supersaturations agree within experimental uncertainties. At activation the droplets are, however, dilute and the water activity coefficients in aqueous solutions of L-glycine provided by Kuramochi et al.[50] show that water activity coefficients and thus van't Hoff factors of 1 is a reasonable assumption for the relevant molalities of L-glycine (<0.15 mol/kg). To our knowledge water activity data for glycyl-glycine are not available.

TABLE 1: Structure, Solubility, Density at 298 K, Molar Mass, and Supplier Information for the Investigated Amino Acids

Compound	Solubility [g/L]	Density [g/cm^3]	Molar mass [g/mol]	Purity	Supplier	Solubility class
 l-glycine	250[a]	1.6[b]	75.07	≥99 %	Sigma Aldrich	High
 glycyl-glycine	230[c]	1.534[d]	132.14	≥99.0 %	Fluka	High
 l-serine	50[e]	1.6[f]	105.09	>99.0 %	Fluka	Intermediate
 l-methionine	10-50[g]	1.22[h]	149.21	>99.0 %	Fluka	Intermediate
 l-glutamic acid	8.6[i]	1.538[j]	147.13	≥99 %	Merck	Low
 l-aspartic acid	5.2[k]	1.645[l]	133.10	≥99 %	Merck	Low
 l-tyrosine	0.47[m]	1.37[n]	181.19	>99.0 %	Fluka	Very low

[a] References 30−34. [b] Reference 35. [c] Reference 36. [d] Reference 37. [e] Reference 31, 32, and 38. [f] Reference 39. [g] Solubility was tested by trying to dissolve L-methionine in Milli-Q water. The visual inspection of the solubility yielded a value between 10 and 50 g/L, where we used 30 g/L in the calculations. [h] Reference 40. [i] Reference 38. [j] Reference 41. [k] Average of refs 33 and 34. [l] Reference 42 [m] Average of refs 33 and 34. [n] Reference 40 reported for DL-tyrosine.

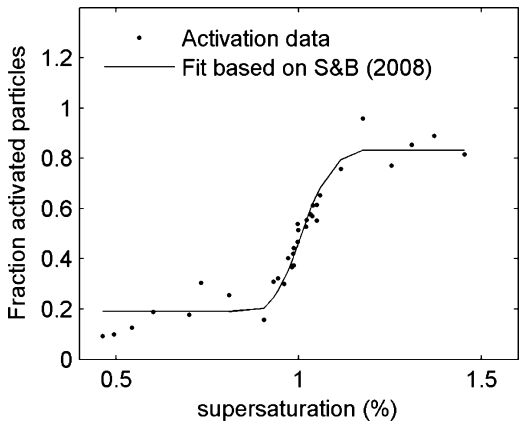


Figure 1. Activation spectrum of 40 nm diameter particles containing a mass fraction of 60% aspartic acid, 20% L-tyrosine, and 20% ammonium sulfate. Shown with dots is the measured activated fraction as a function of calibrated supersaturation and a solid line representing the fit based on Svenningsson and Bilde (S&B).[43]

Finally, the underprediction by the Köhler model may be related to uncertainty in the density values used to calculate the Köhler curve. The densities of L-glycine and glycyl-glycine would have to be roughly 15% lower than those given in Table 1 to obtain a result similar to the van't Hoff factors being set to 0.87. Considering the low precision of density data in Table 1, this is not a very unlikely scenario. In conclusion it is reasonable to expect that the underprediction of the experimental results by the Köhler model is caused by a combination of several factors including surface tension, nonideality, and uncertainties in the available density data.

L-Serine and L-methionine belong to the group of intermediate solubility compounds, and Köhler theory predicts different values for the limited and full solubility cases in the investigated particle size range (50−140 nm diameter). The measurements presented in Figure 2c indicate that L-serine behaves as if fully soluble during the experiments although the critical supersaturation values calculated with the full solubility Köhler model are slightly underpredicted. Once more, a 15% decrease in the density reported in Table 1 would bring the calculated Köhler line to agree with all measurements within experimental uncertainties. No measurement data for L-methionine are shown since particles of L-methionine appeared to be difficult to activate at supersaturations up to 1.5% (the upper limit in this study) and results were not reproducible between consecutive measurements. The theoretical critical supersaturation for a 100 nm diameter particle of L-methionine is 1.8% when accounting for

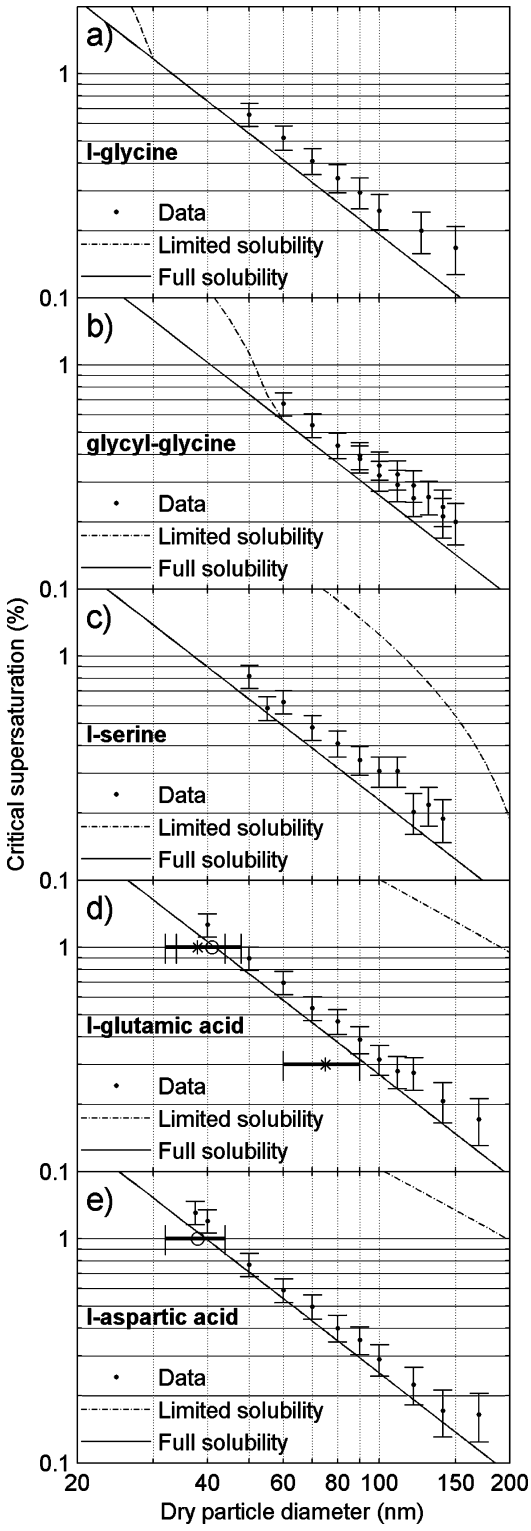


Figure 2. Measured critical supersaturations (*Sc*) for five pure amino acids compounds as a function of dry size. Corresponding model results according to eqs 1−4 for the different compounds assuming limited and full solubility are also shown. The compounds are (a) L-glycine, (b) glycyl-glycine, (c) L-serine, (d) L-glutamic acid, and (e) L-aspartic acid, where solubility decreases from panels a to e. Stars represent measured data from Raymond and Pandis,[41] whereas open circles represent measured data from Huff-Hartz et al.[42]

limited solubility. Thus, activation is not expected if limited solubility has an effect, since we are not able to measure above 1.5% supersaturation. Particles of the low solubility compounds, L-glutamic acid (Figure 2d) and L-aspartic acid (Figure 2e),

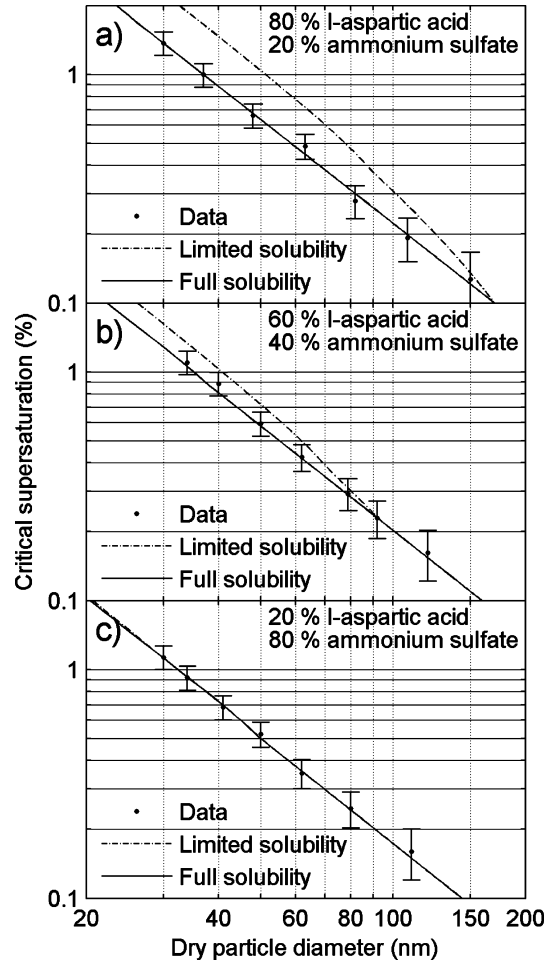


Figure 3. Measured *Sc* as a function of dry particle size for mixed particles of L-aspartic acid and ammonium sulfate: (a) 80% L-aspartic acid/20% ammonium sulfate (by mass), (b) 60% L-aspartic acid/40% ammonium sulfate, and (c) 20% L-aspartic acid/80% ammonium sulfate. Corresponding model results according to eqs 1−4 for the different mixtures assuming limited and full solubility are also shown. In the case of limited solubility the solubility of both compounds is included in the calculation.

activate readily in reasonable agreement with Köhler theory assuming full water solubility. As can be seen in Figure 2 and Table 2, the data are consistent with results by Raymond and Pandis[41] and Huff-Hartz et al.[42]

Particles of pure L-tyrosine, which belongs to the very low solubility group, appeared to be difficult to activate up to a supersaturation of 1.5%, and the results were not reproducible between consecutive measurements. Hence, L-tyrosine behaved in much the same way as L-methionine and L-tyrosine is also not expected to activate with our instrument setup if limited solubility is important. The nonreproducibility of the two compounds may be related to the presence of trace amounts of impurities as explained in Bilde and Svenningsson.[19] For a 100 nm particle of L-methionine or L-tyrosine, a 1% soluble impurity (with properties similar to NaCl) would decrease the critical supersaturation from ∼1.8% to ∼0.75% and from ∼2.1% to ∼1.4%, respectively, when calculated with the limited solubility Köhler model.

Huff-Hartz et al.[42] examined a variety of pure organic compounds in addition to the two amino acids presented here and concluded that with few exceptions, only compounds with a very low solubility are activating in accordance with Köhler theory accounting for limited solubility. Above water solubilities

TABLE 2: A Comparison of Data from This Study with Literature Data[a]

	this study				Raymond and Pandis[41]		Huff-Hartz et al.[42]	
species	dry size (nm)	*Sc* (%)	model full sol.[b]	model lim. sol.[c]	dry size (nm)	*Sc* (%)	dry size (nm)	*Sc* (%)
L-glutamic acid	40	1.26 ± 0.16	1.1	5.3	38 ± 6	1.0	42 ± 7	1.0
L-aspartic acid	40	1.20 ± 0.14	1.0	5.3			38 ± 6	1.0

[a] The dry diameter required to observe a CCN activation of 50% of the pure particles at around 1% supersaturation (*Sc*) is presented. Predictions from Köhler theory are included for comparison. [b] Köhler model assuming full solubility. [c] Köhler model assuming limited solubility.

of 3 g/L, most compounds behave as if fully soluble although they are not expected to be fully dissolved at the point of activation. Our study concurs with the latter conclusion (with the possible exception of L-methionine) and therefore we believe that the majority of amino acids can be added to the class of organic compounds following this solubility behavior.

Bilde and Svenningsson[19] show that soluble impurities may significantly impact the cloud droplet activation of single component particles of limited solubility and make them activate as if fully soluble. To explain why pure particles of L-serine, L-glutamic acid, or L-aspartic acid activate as if fully soluble, mass fractions between 10% and 30% (of a molecule with the properties of sodium chloride) would, however, be needed. Impurities could stem from tubing or the chemicals and water used. All tubing was carefully cleaned prior to experiments and based on the purity of our compounds and the use of Milli-Q water in all experiments such large amounts of impurities should not be present. We therefore disregard impurities as a reasonable explanation for the observed fully soluble behavior. We can, however, not rule out that impurities might to some extent increase the solubility of the L-serine, L-glutamic acid, and L-aspartic acid particles.

Huff-Hartz et al. hypothesize that the particles are never really dry in their system despite that they are measuring at humidities around 5%, and therefore the particles activate as if fully soluble. Since we were measuring at humidities below or around 6% this can also be the case in our system. Padro et al.[51] further speculate that curvature-enhanced solubility might be important (described in Padro and Nenes[52]).

4.2. Mixtures. The CCN activity of a number of mixtures of ammonium sulfate and amino acids with either low solubility or very low solubility were also investigated in this work.

Since the activation behavior of pure L-aspartic acid particles was reproduced well by Köhler theory assuming full solubility, we expected that mixtures of this compound with ammonium sulfate would also behave as if fully soluble. To verify this hypothesis, dried mixed particles containing 20%, 40%, and 80% ammonium sulfate respectively (the percentages refer to the mass of the dry particle) were investigated. Another goal of the experiments was to see if any effect of the salt on the water solubility or surface tension of the amino acid during cloud droplet activation could be inferred from a comparison of measured and calculated critical supersaturations.

A change in solubility of amino acids in the presence of ammonium sulfate has been observed in bulk solutions where ammonium sulfate is able to both increase and decrease water solubility of the organic depending on the molality of the solution (salting in and salting out effect respectively).[53] The salt may also force the organic compound to partition to the surface, which decreases the surface tension beyond that of the pure organic compound in a solution of similar concentration.[51,54,55] The surface tension effect is stronger at higher salt concentrations, and is thus expected to be most pronounced for the mixed particles containing 80% ammonium sulfate.

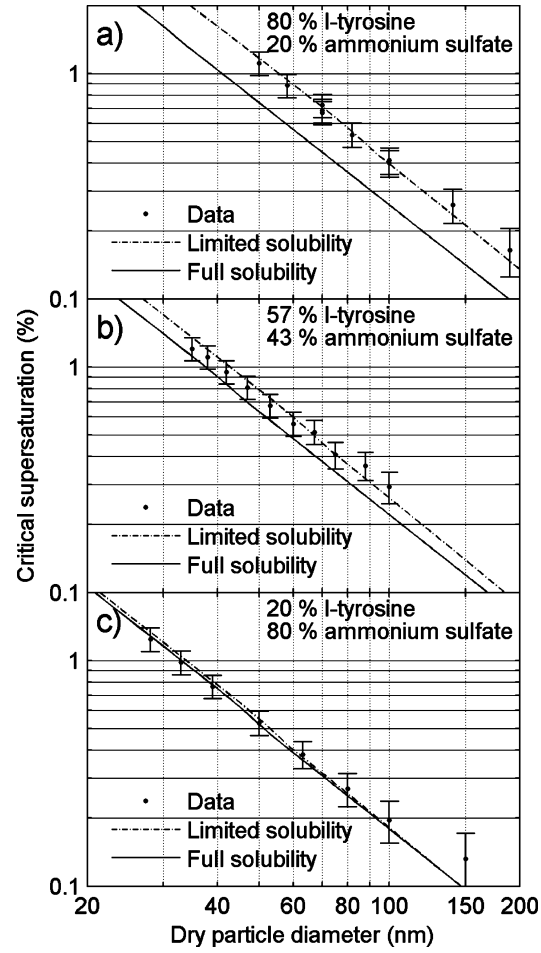


Figure 4. Measured *Sc* as a function of dry particle size for three mixed particles of L-tyrosine and ammonium sulfate: (a) 80% L-tyrosine/20% ammonium sulfate (by mass), (b) 57% L-tyrosine/43% ammonium sulfate, and (c) 20% L-tyrosine/80% ammonium sulfate. Corresponding model results according to eqs 1−4 for the different mixtures assuming limited and full solubility are also included.

Figure 3 shows *Sc* vs. dry particle size for the three mixtures of L-aspartic acid and ammonium sulfate. All particles activate according to Köhler theory assuming full solubility as expected and we see no evidence that salting in/salting out or surface tension affects critical supersaturations.

Results for mixtures of L-tyrosine and ammonium sulfate are presented in Figure 4. For 80% L-tyrosine and 20% ammonium sulfate, the activation follows the limited solubility path (Figure 4a). For the 57% L-tyrosine case, the relatively large uncertainty of the measurement values compared to the proximity of the limited and full solubility Köhler model lines does not allow us to tell if the activation is limited by solubility (Figure 4b). For the lowest mass fractions of L-tyrosine studied (20%) the full solubility and limited solubility lines fully coincide at the investigated diameters and agree with the measured critical supersaturation (Figure 4c).

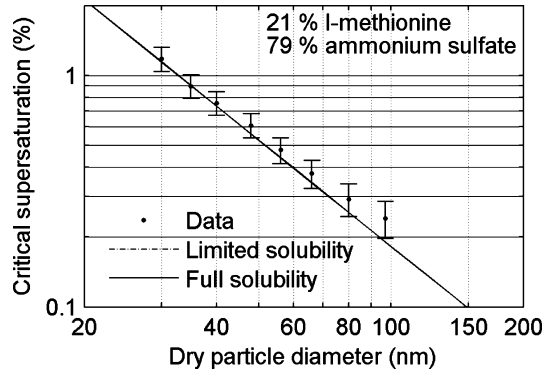


Figure 5. Measured *Sc* as a function of dry particle size for the mixture of 21% L-methionine and 79% ammonium sulfate as well as corresponding model results according to eqs 1−4 for the mixture assuming limited and full solubility. The limited and full solubility lines coinside, and hence the dashed line representing the limited solubility case is not visible.

As with pure L-methionine, particles containing 60% L-methionine and 40% ammonium sulfate seemed difficult to activate below 1.5% supersaturation, and again the results were not reproducible. This may be related to solubility effects and uncertainties in our knowledge about the water solubility of L-methionine. We have estimated the solubility of L-methionine in water, but this is only a crude estimate and better determinations of the solubility of L-methionine in aqueous solution and in aqueous solution containing ammonium sulfate would be needed to understand the behavior of these particles. We cannot exclude that surface tension, water−solute, organic−inorganic interactions, or even dissolution kinetics could also play a role. For example, the Asa-Awuku and Nenes[56] study on model compounds shows that the critical supersaturation can potentially increase and that activation can be delayed as the migration of dissolved inner core material toward the droplet surface is slow enough to allow for a more dilute droplet close to the droplet surface. For particles containing 20% L-methionine and 80% ammonium sulfate all results were reproducible and the particles activated according to Köhler theory as can be seen from Figure 5.

For mixed particles containing L-tyrosine or L-methionine together with ammonium sulfate it is interesting to notice that there is a systematic shift in measurements to activate at a higher critical supersaturation than predicted by Köhler theory for the largest dry particle diameters. This could be related to a change in water activity as the droplet dilution at activation increases with increasing dry particle diameter. It is, however, not clear why water activity would decrease with increasing dilution.

For the ternary dry particles dominated by L-aspartic acid (60% L-aspartic acid, 20% L-tyrosine, and 20% ammonium sulfate) activation follows Köhler theory assuming full solubility, whereas particles activate according to the limited solubility Köhler theory for the mixture with 61% L-tyrosine, 19% L-aspartic acid, and 20% ammonium sulfate (Figure 6). Again it seems that a solid core is established and maintained during activation only for large mass fractions of L-tyrosine.

It is interesting to compare Figure 6a (61% L-tyrosine, 19% L-aspartic acid, and 20% ammonium sulfate) with Figure 4b (57% L-tyrosine, 43% ammonium sulfate): the replacement of ammonium sulfate with the same mass fraction of L-aspartic acid results in an increase in critical supersaturation consistent with Köhler theory accounting for limited solubility for both L-tyrosine and L-aspartic acid.

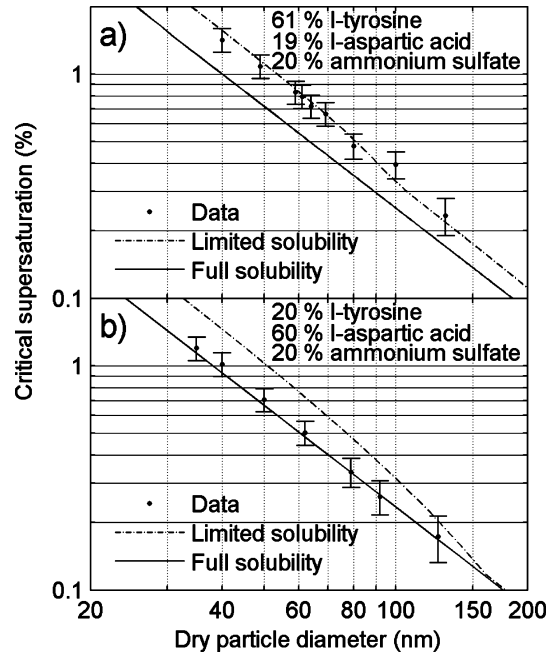


Figure 6. Measured *Sc* as a function of dry particle size for two ternary mixed particles: (a) 61% L-tyrosine/19% L-aspartic acid/20% ammonium sulfate (by mass) and (b) 20% L-tyrosine/60% L-aspartic acid/20% ammonium sulfate. Corresponding model results according to eqs 1−4 for the different mixtures assuming limited and full solubility are also shown.

In other words; for mixtures with the very low solubility compound L-tyrosine occupying 60% or more of the total mass, the activation tends to be limited by solubility.

5. Conclusions

We have studied the CCN activity of a series of single component dried amino acid particles as well as dry mixed particles composed of one or two amino acids internally mixed with ammonium sulfate.

The high solubility (>100 g/L) pure L-glycine and glycylglycine particles activated as if they were fully soluble, although critical supersaturations were slightly underpredicted by Köhler theory. The intermediate solubility (10−100 g/L) L-serine particles and the low solubility L-glutamic acid and L-aspartic acid particles activated as if they were fully soluble even though Köhler theory accounting for limited solubility predicts that the activation of these compounds should be limited by solubility. Plausible explanations for this might be that curvature-enhanced solubility played a role,[51,52] or that the particles were not completely dry.[42]

Pure L-tyrosine and L-methionine proved difficult to study and our results are inconclusive, possibly due to an effect of limited solubility and/or to trace amounts of soluble impurities.

In mixed particles containing one or two amino acids and ammonium sulfate it seems that at least 60% of an amino acid with very low solubility (L-tyrosine) is needed to form and maintain a solid core in the activation process. In this case the activation is limited by solubility. In all other cases the mixed particles activated according to Köhler theory assuming full solubility. The mixed particles containing 60% L-methionine and 40% ammonium sulfate proved difficult to study. We cannot exclude that surface tension, water−solute, organic−inorganic interactions, or even dissolution kinetics could influence the activation process and explain these difficulties.

Atmospheric particles are mixtures of organic and inorganic material and it does not seem likely that a single particle will contain 20% or more by mass of low solubility amino acids. On the basis of our results we therefore conclude that in most mixed particles of atmospheric relevance the amino acids we have studied will be effective CCN material.

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