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Estimating aqueous solubility and hygroscopicity of amino acid particles with COSMOtherm

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Amino acids are the primary form of nitrogen in atmospheric aerosol particles. Understanding their aqueous solubility and hygroscopicity is essential for examining their interaction with water vapor and their role in regulating the atmosphere-biosphere nutrient cycle. We use the conductor-like screening model for real solvents (COSMO-RS) to investigate a group of amino acids and their mixtures with inorganic salts. Unlike other thermodynamic models, COSMO-RS allows for property calculations of amino acid groups and of zwitterionic forms. Salting-out effects are observed for most of the amino acids. There is good agreement between the model-derived water activity and measurement values from the literature, highlighting the importance of including zwitterions in the model. Using the model-derived water activity and Köhler theory, we compute the cloud droplet activation curves and find that the amino acids, with 1:1 mass ratio, increase the critical supersaturation of ammonium sulfate or sodium chloride particles by less than 0.15%-points.

Atmospheric aerosol particles consist of a myriad of inorganic and organic species. Amino acids contain amino and carboxylic acid functionalities and are considered to be one of the major forms of organic nitrogen in atmospheric aerosol particles. Thus, they importantly regulate the nutrient cycle between the atmosphere and the biosphere^{1,2}. To date, a variety of amino acids have been identified in different environments across forest^{3,4}, coastal^{2,5}, polar^{6,7}, rural⁸, and urban areas⁹⁻¹¹. The ubiquity of amino acids in the atmosphere underscores their importance in the global nitrogen cycle.

The extent to which amino acids interact with water vapor at different relative humidities (RH) influences their chemical reactivity and potential for cloud formation, ultimately affecting their behaviors in the atmosphere. Thus, it is crucial to understand the physicochemical properties (e.g., solubility, activity) describing the interactions of amino acids with water. A range of experimental studies have measured the aqueous solubilities of amino acids in pure water and in aqueous solutions containing inorganic salts¹²⁻¹⁵. In addition, the water activities (α_w) of amino acids under sub-saturated conditions (RH < 100%) have been reported in multiple studies using either bulk solutions¹⁶⁻¹⁸ or aqueous particles^{19,20}.

Efforts have been spent on modeling the RH-dependent activity coefficients of organics using thermodynamic models, such as UNIQUAC Functional-group Activity Coefficients (UNIFAC)²¹, Aerosol Inorganic-Organic Mixtures Functional Groups Activity Coefficients (AIOMFAC)²²⁻²⁴, and the conductor like screening model for real

solvents (COSMO-RS)²⁵⁻²⁷. While UNIFAC and AIOMFAC are group-contribution-based approaches, COSMO-RS is based on quantum chemical calculations. Previous comparisons have demonstrated that both AIOMFAC and COSMO-RS can provide similar α_w estimates for inorganic ammonium salts²⁸ and carboxylic acids^{29,30}. While the group contribution calculations take only seconds, UNIFAC and AIOMFAC are able to model only a limited set of functionalities. In contrast, while requiring hours with a single processor for quantum chemistry calculations at substantial computational cost, COSMO-RS can model any functionalities. For example, we recently use COSMO-RS to explore the α_w for a set of aminium²⁸ and organosulfur³¹ compounds of atmospheric importance^{32,33}. Compared with the hygroscopicity measurements of organosulfur compounds from multiple studies³⁴⁻³⁷, the hygroscopicity estimates based on the COSMO-RS derived α_w have shown a good agreement, with $\pm 5\%$ relative differences³¹.

Until now, Marsh et al.²⁰ is the only study modeling the water uptake of amino acids. Unfortunately, their predictions using UNIFAC consistently underestimate the water uptake for the ten studied amino acids, likely because the zwitterionic forms of amino acids were not considered by UNIFAC. As a quantum chemistry model, COSMO-RS can use multiple conformers at the lowest chemical potential as inputs and allows for the inclusion of zwitterions for amino acids in the α_w calculations. Here, we perform thermodynamic property calculations with the COSMOtherm

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Table 1 | Properties of the studied amino acids

Amino acid	Chemical formula	MW (g mol ⁻¹) ^a	ρ (g cm ⁻³) ^b	ρ_{exp} (g cm ⁻³)	Hydropathy index
Hydrophilic					
L-asparagine	C ₄ H ₈ N ₂ O ₃	132.12	1.290	1.543	-3.5
L-aspartic acid	C ₄ H ₇ NO ₄	133.10	1.248	1.660	-3.5
L-glutamine	C ₅ H ₁₀ N ₂ O ₃	146.14	1.169	1.364	-3.5
L-lysine	C ₆ H ₁₄ N ₂ O ₂	146.19	0.900	-	-3.9
L-arginine	C ₆ H ₁₄ N ₄ O ₂	174.20	1.000	1.560	-4.5
Neutral					
L-glycine	C ₂ H ₅ NO ₂	75.07	1.385	1.161	-0.4
L-serine	C ₃ H ₇ NO ₃	105.09	1.325	1.600	-0.8
L-proline	C ₅ H ₉ NO ₂	115.13	1.341	1.064	-1.6
L-threonine	C ₄ H ₉ NO ₃	119.12	1.254	1.077	-0.7
L-histidine	C ₆ H ₉ N ₃ O ₂	155.15	1.327	1.449	-3.2
Hydrophobic					
L-alanine	C ₃ H ₇ NO ₂	89.09	1.265	1.432	1.8
L-valine	C ₆ H ₁₁ NO ₂	117.15	1.128	1.230	4.2

^aMolecular weight.^bCOSMOtherm-derived liquid density.

program³⁸, which has the most advanced COSMO-RS implementation allowing the inclusion of multiple conformers, to investigate the solubility and α_w for a set of atmospherically relevant amino acids as summarized in Table 1. For the studied amino acids, a handful of experimental studies have reported their aqueous solubilities^{12–15,39,40}, and α_w ^{16–20}, allowing comparisons with the predicted values from COSMOtherm. Furthermore, we predict the hygroscopic growth and cloud droplet activation of the studied amino acids when mixed with ammonium sulfate ((NH₄)₂SO₄) and sodium chloride (NaCl), which are the two main inorganic salts in atmospheric aerosol particles.

Results

Aqueous solubility

We estimate the relative solubilities of individual amino acids in aqueous solutions with up to 5 mol kg⁻¹ of an inorganic salt, using the solubility of the salt in pure water as the reference. Apart from (NH₄)₂SO₄ and NaCl, we include two other chloride-containing inorganic salts for investigation, potassium chloride (KCl) and ammonium chloride (NH₄Cl), which can be found in atmospheric aerosol particles. Figure 1 shows the relative solubility estimates for the amino acids categorized according to the hydropathy classes of their side chains.

In the hydrophilic group, the addition of higher amounts of inorganic salts into the solution decreases the solubilities of L-aspartic acid, L-lysine, and L-arginine (i.e., salting out). However, among the same group, the solubilities of L-asparagine and L-glutamine increase with higher amounts of inorganic salts (i.e., salting in), which are relatively less hydrophilic than the three other amino acids. Furthermore, in the neutral and hydrophobic groups, increasing amounts of inorganic salts either decrease or do not change the solubilities of the amino acids.

For each amino acid, similar degrees of salting-in or salting-out effects are observed between the three chloride-containing inorganic salts. This suggests that when Cl⁻ is the anion in the aqueous solution, each of the three cations plays a negligible role in the dissolution of amino acids in pure water. Among the four chosen inorganic salts, (NH₄)₂SO₄ exerts the strongest salting-out effect or the weakest salting-in effect on the amino acids. Such effects are very likely due to the presence of SO₄²⁻ when comparing the results associated with (NH₄)₂SO₄ and NH₄Cl. An exceptional case is observed in L-histidine. Its solubility increases strongly with a higher content of (NH₄)₂SO₄.

Water activity (α_w)

The α_w value of each studied amino acid is calculated with the water mass fraction (m_w) ranging from 0 to 1, assuming complete dissolution of the amino acids in water. Here, utilizing m_w for the analysis allows direct comparison of α_w across the studied amino acids with different molecular weights. The corresponding α_w estimates (dashed lines) together with the experimental data on the bulk solutions and aqueous particles of pure amino acids from the literature are shown for the three groups of amino acids in Fig. 2. Note that in aqueous solutions, amino acids can form zwitterions that contain equal numbers of positively and negatively charged functional groups. Therefore, we perform two different types of α_w estimates: one (neutral-type) using neutral forms of amino acids and the other (mixed-type) using both their neutral and zwitterionic forms.

At any of m_w below 0.5, the mixed-type estimate consistently provides a lower α_w value than the neutral-type one for individual amino acids. In other words, the presence of zwitterions of amino acids in aqueous solutions increases their water uptake. This is because zwitterionic amino acids have larger charged surface areas than their neutral forms, attracting polar water molecules. However, when m_w is 0.5 or above, the two types of COSMOtherm estimates start to merge together and show almost identical α_w values for each amino acid. This is reasonable since the surface charges of the amino acids have only a small effect on the total surface charge distribution of the dilute solutions. Moreover, when compared to the literature data, the two types of COSMOtherm estimates well agree with those measured in the bulk solutions^{16–18}, which typically have the equilibrium α_w close to 1. However, compared to those measurements of aqueous particles, only the mixed-type estimates that accounted for the presence of zwitterions of amino acids give a good agreement within the range of the measured α_w between 0.45 and 0.99.

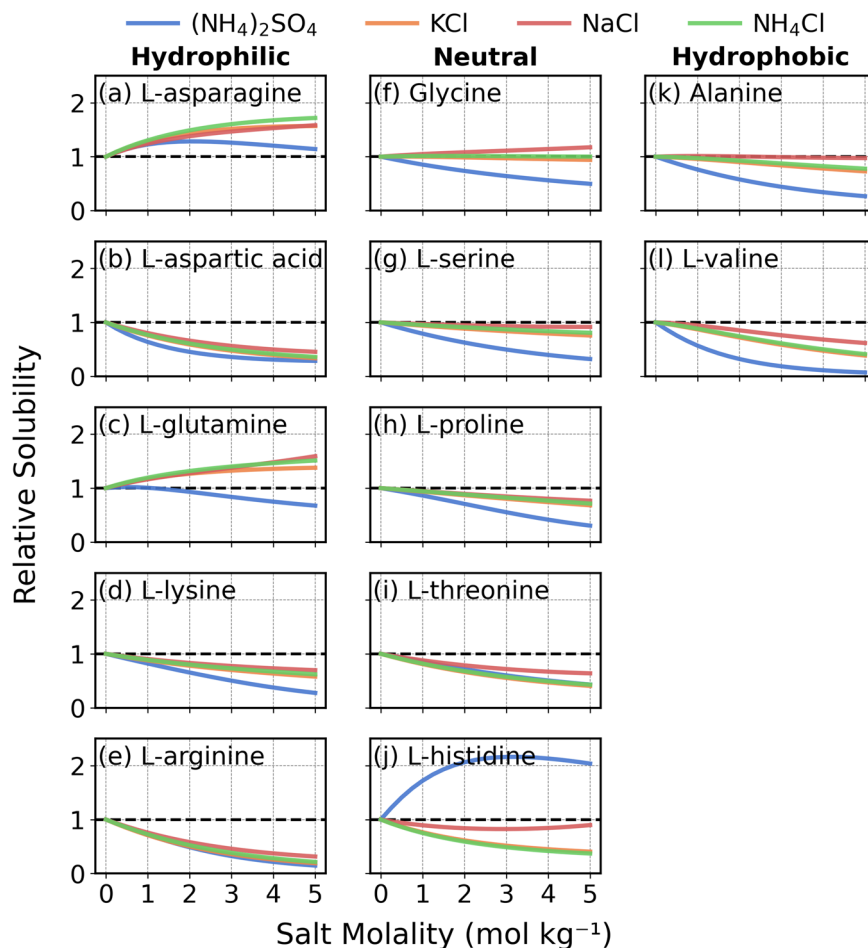
For the studied amino acids, we are interested in their degree of aerosol water uptake, especially at a high α_w , where aerosol light scattering effect can be important. Therefore, with the aid of Eqs. (1)–(6), we estimate the corresponding hygroscopicity parameters expressed in κ ⁴¹ at α_w of 0.95, as summarized in Supplementary Table 1. According to the estimated κ , the studied amino acids, except L-lysine, show moderate hygroscopicity in the range of 0.12–0.28. No clear trend of κ exists among the three hydropathy classes; instead, a decrease in κ is observed with increasing molecular volumes of amino acids (Supplementary Fig. 1).

Cloud droplet activation

To determine the critical supersaturation (SS_{crit}) of the amino acid and amino acid-salt mixture particles, we analytically solve the Köhler equation expressed as Eq. (7) to generate the Köhler curves over a range of wet droplet diameters (D_{wet}). The comparison between E-AIM and COSMOtherm in Supplementary Fig. 2 shows that both of the thermodynamic models can provide very similar Köhler curves for (NH₄)₂SO₄ and NaCl dry particles with a diameter of 50 nm.

Figure 3 shows the Köhler curves and bulk compositions for the glycine particles and glycine-salt mixture particles (i.e., glycine-(NH₄)₂SO₄) and glycine-NaCl) at a mass ratio of 1:1 with a dry particle diameter (D_{dry}) of 50 nm. For pure glycine particles, the corresponding SS_{crit} is 0.63%. When glycine is mixed with either (NH₄)₂SO₄ or NaCl in the particles, we observe decreases in SS_{crit} compared to the pure glycine particles. Note that we assume a negligible difference in Kelvin effects between glycine particles and glycine-salt mixture particles, as the studied amino acids are weakly surface-active ($\approx 71 \text{ N m}^{-1}$)⁴². Therefore, the observed changes in SS_{crit} after the addition of inorganic salts are attributed to the strong water uptake of inorganic salts and consequent increases in D_{wet} at a fixed α_w , as suggested by the curves representing the Raoult effects (Fig. 3c, e, g, i). In either particles mixed with (NH₄)₂SO₄ or NaCl, we observe lower values of SS_{crit} with a higher mass fraction of inorganic salts, which is caused by the stronger hygroscopicity of the two inorganic salts compared to glycine. Similar levels of decrease in SS_{crit} are also observed after the addition of (NH₄)₂SO₄ or NaCl in the particles containing amino acids other than glycine (Supplementary Figs. 3 and 4).

Fig. 1 | Relative solubilities of amino acids with inorganic salts. Relative solubilities of amino acids in the hydrophilic (a–e), neutral (f–j) and hydrophobic groups (k, l), in the presence of four different inorganic salts (in color) with salt molality of 0–5 mol kg⁻¹.



Discussion

Amino acids are one of the underexplored atmospheric compound classes using thermodynamic models, due to the lack of parameterization of amino acid groups and the difficulty of incorporating their zwitterionic forms. In this study, we use COSMOtherm calculations to estimate the aqueous solubility and hygroscopicity for 12 amino acids that are commonly found in ambient atmospheric aerosol particles^{2–11}. Using COSMOtherm enables accounting for the zwitterionic forms of amino acids, which have larger charged surface areas for attractive interaction with water molecules than the charge-neutral forms. Overall, the COSMOtherm estimates agree well with the literature α_w data measured in bulk solution^{16–18} and aqueous particles^{19,20}, for most of the studied amino acids. The importance of including the zwitterionic form of the amino acids in COSMOtherm calculations is especially apparent from the comparison of calculated and experimental α_w for mixtures with high mass fractions of amino acids. Along with our previous studies comparing COSMOtherm-derived α_w of various atmospherically relevant organic compound classes (organosulfur compounds³¹, aminium salts²⁸ and carboxylic acids^{29,30}) with experiments, our calculations show the suitability of COSMOtherm to estimate water uptake and hygroscopicity.

To investigate the degree of water uptake for individual amino acids at a certain RH, we express their hygroscopicity with κ at 95% RH and observe an association between increasing molecular volume and decreasing κ . A similar pattern is also reported in a previous hygroscopicity measurement of dicarboxylic acids and sugars with solubility larger than $7 \times 10^{-1} \text{ g ml}^{-1}$ ¹⁴³. Regarding the κ values for the amino acids, a broad agreement is found between this study and Marsh et al.²⁰, given the differences in the density values of amino acids used in the two studies (Supplementary Table 1). A further comparison between this study and Hyttinen²⁸ shows that when present as sulfate salts, the selected

amino acids overall exhibit substantially low κ values (Supplementary Table 1), aligning with their decreased solubilities with higher amounts of $(\text{NH}_4)_2\text{SO}_4$, as demonstrated in Fig. 1.

The addition of the selected inorganic salts is estimated to drive salting out for most of the amino acids but salting in for L-asparagine and L-glutamine. The three chloride-containing inorganic salts (i.e., KCl, NaCl, and NH_4Cl) show similar salting effects. In comparison, $(\text{NH}_4)_2\text{SO}_4$ exhibits a stronger salting-out effect or a weaker salting-in effect for amino acids, possibly driven by SO_4^{2-} . Note that the four different inorganic salts of interest come from different emission sources. For example, $(\text{NH}_4)_2\text{SO}_4$ is typically found in aerosol particles influenced by anthropogenic emissions of ammonia and sulfur. Concerning the three chloride-containing salts, the one with Na^+ can originate from sea spray, the one with NH_4^+ can result from biomass burning, and the one with K^+ can arise from both sources of emissions. Thus, the aqueous solubilities of amino acids in atmospheric aerosol particles can differ based on the type and intensity of the air masses that they encounter.

The salting-out effect caused by inorganics can potentially lead to liquid-liquid phase separation (LLPS) in aqueous amino acid-salt particles, forming an outer layer of amino acids and an inner inorganic core. The LLPS is very likely to occur under subsaturated conditions ($\text{RH} < 100\%$) when aqueous particles are highly concentrated, and salt molality is high. As the amino acid is weakly surface-active ($\approx 71 \text{ N m}^{-1}$)⁴², the amino acid present at the droplet surface is not expected to depress the surface tension. It is therefore unlikely that the surface tension of amino acid-containing particles would have an effect on the hygroscopicity and cloud condensation nuclei (CCN) activity. Additionally, the LLPS within amino acid-salt particles might have a negligible impact on the particle hygroscopicity through changes in water activity, as LLPS is unlikely to influence the surface tension. On the other hand, a fast oxidation kinetics of amino acids through

Fig. 2 | Water activities (α_w) for aqueous solutions of amino acids. COSMOtherm-derived and literature α_w for aqueous solutions of the amino acids in the hydrophilic (a–e), neutral (f–j) and hydrophobic (k, l), as a function of water mass fraction (m_w) at 295 K. The black and grey dashed lines stand for COSMOtherm-derived estimates with and without considering the zwitterionic forms of amino acids, respectively. The red and blue markers represent literature data measured using bulk solutions^{16–18} and aqueous particles^{19,20}, respectively.

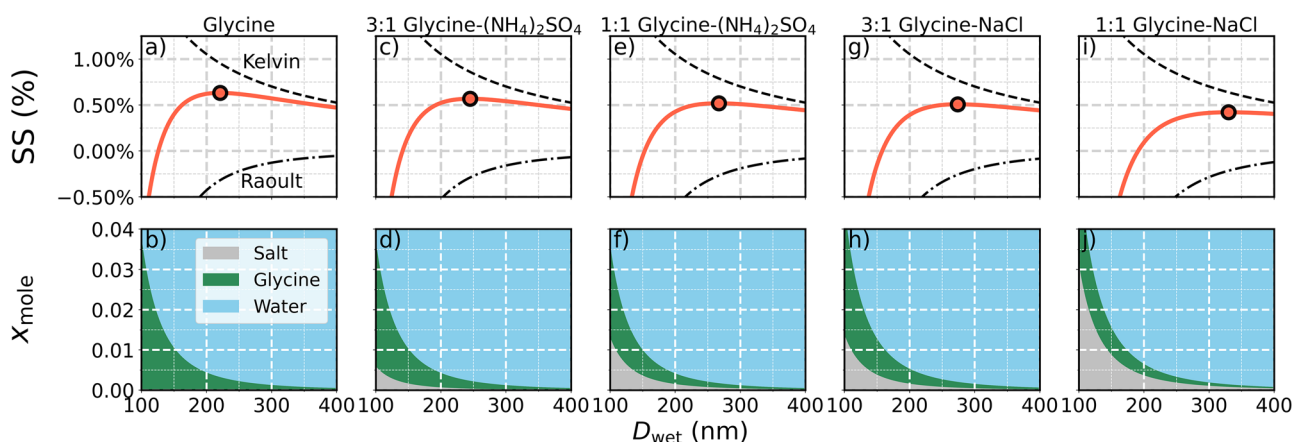
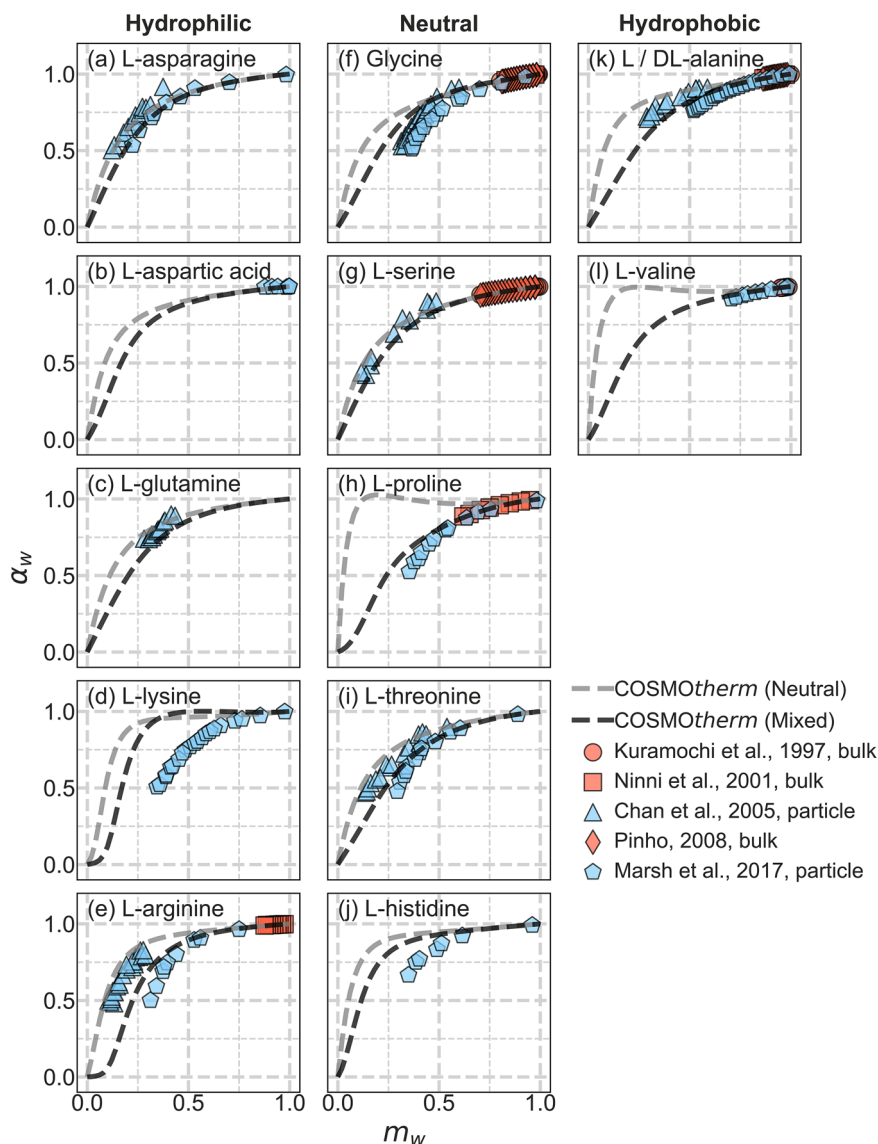


Fig. 3 | Cloud droplet activation simulations of pure glycine particles and glycine-salt particles. Köhler curves (top row) and bulk compositions (bottom row) for the particles of pure glycine (a, b), its mixture with $(\text{NH}_4)_2\text{SO}_4$ (c–f) or

NaCl (g–j) in 3:1 and 1:1 mass ratios, with a dry particle size of 50 nm in diameter. The filled circles on the Köhler curves indicate the estimated critical supersaturation (SS).

heterogeneous oxidation might occur due to the enrichment of the amino acids and enhanced adsorption of hydroxyl radicals at the particle surface⁴⁴.

Following Köhler theory, we first determine how the SS_{crit} values vary between amino acid particles and amino acid-salt mixture particles with D_{dry} of 50 nm. Across the studied amino acids, we observe similar levels of decreases in the SS_{crit} when they are mixed with $(NH_4)_2SO_4$ or NaCl, and such a decrease in the SS_{crit} becomes stronger with increasing mass ratios of inorganic salts, as demonstrated in Supplementary Figs. 3 and 4. To illustrate the impact of amino acids on CCN activity, we compare the SS_{crit} of amino acid-salt mixture particles to those of pure inorganic salts across different D_{dry} . We further estimate the difference in SS_{crit} (ΔSS_{crit}) of each amino acid between its mixture with $(NH_4)_2SO_4$ or NaCl and the corresponding pure inorganic salt particles over a range of D_{dry} , from 50 to 300 nm. We also estimate the ΔSS_{crit} between pure amino acid particles and pure inorganic salt particles, which can be considered as the upper limit of ΔSS_{crit} with increasing mass fraction of amino acid in the particles.

Figure 4 shows the median values and interquartile ranges of ΔSS_{crit} for the studied amino acids. The values of ΔSS_{crit} decrease with higher D_{dry} , due to the higher solute content and lower α_w at a fixed D_{wet} . The dependence of changes in ΔSS_{crit} on D_{dry} is very similar between the two types of amino acid-salt particles in a mass ratio of 1:1. When the mass ratio between amino acids and salts is 3:1, we observe larger values of ΔSS_{crit} for the amino acid particles mixed with NaCl, compared to those mixed with $(NH_4)_2SO_4$. Such a difference in ΔSS_{crit} between these two types of amino acid-salt particles is expected to become larger, as the estimate for pure amino acid particles can be assumed as the upper ΔSS_{crit} limit with increasing mass fraction of amino acid in the particles. As mentioned above, NaCl typically originates from sea spray in marine environments, while $(NH_4)_2SO_4$ can be found in aerosol particles influenced by anthropogenic emissions. Even contributing to a similar fraction in mass in particles, the degree to which amino acids affect cloud droplet activation can depend on the D_{dry} and the type of co-present inorganic salts.

In conclusion, COSMOtherm can incorporate the zwitterionic forms that are currently underexplored in other thermodynamic models. The model provides accurate hygroscopicity estimates of the studied amino acids against the literature and provides insights into how their presence affects the CCN activity of inorganic salts. COSMOtherm can be a useful tool to generate valuable data of α_w for a large dataset of amino acids of atmospheric relevance, potentially helping to understand their role in aerosol-cloud interaction and in regulating the nutrient cycle between the atmosphere and the biosphere.

Methods

COSMO-RS calculations

Water activities and solubilities are calculated using the COSMO-RS^{25–27} implemented in the COSMOtherm program³⁸. Activity coefficients are calculated assuming that all components are in a mixed aqueous phase (i.e., amino acids are dissolved in water). For relative solubilities, we give experimental aqueous solubilities of the amino acids as a reference and estimated solubilities in salt solutions using the solid-liquid equilibrium solver (SLESOL). The free energy of the fusion of each amino acid is estimated from the reference solubility. Other additional experimental data are therefore not needed in the relative solubility calculations.

Out of the studied amino acids, only glycine is included in the COSMObase, a database of input files for COSMOtherm calculations. Additionally, the input files of all of the inorganic species of this study are taken from the COSMObase. For the other amino acids, all conformers are sampled using the Spartan 24 program⁴⁵ and the MMFF method. Then, single-point COSMO calculations are performed at the BP/SV(P) level of theory using the COSMOconf and TURBOMOLE programs after which, similar conformers are omitted based on equal chemical potentials. The geometries of the remaining conformers are optimized at the BP/SV(P) and BP/TZVP levels of theory, with duplicate conformers omitted after each optimization based on similarities in chemical potential and geometry. Final single-point energies are computed at the BP/TZVPD-FINE level of theory.

In COSMObase, the conformer set of glycine includes one zwitterionic conformer and five neutral conformers. We therefore perform

separate conformer searches and density functional theory calculations for the neutral-form and zwitterionic amino acids, considering all options of hydrogen shift when the amino acid contains multiple acid groups or amino groups (e.g., asparagine). The COSMOtherm calculations are run using two different conformer sets: one with only neutral-form conformers and the other with both the neutral-form and zwitterionic amino acids. This is done to test the ability of COSMOtherm to estimate the thermodynamic properties without and with the zwitterionic conformers.

In COSMOtherm, α_w is calculated using the BP_TZVPD_FINE_24 parameterization. Relative solubility calculations are performed using the BP_TZVP_ELYTE_24, which takes into account the ionic interaction of small ions, such as Na^+ , K^+ and SO_4^{2-} .

Estimating aerosol particle hygroscopicity

Petters and Kreidenweis⁴¹ introduced a hygroscopicity parameter, κ , to describe the degree of aerosol water uptake at a certain α_w . When in equilibrium with surrounding RH, the α_w of aerosol particles can be expressed using the hygroscopic growth factor (HGF) as follows:

$$\alpha_w = \frac{HGF^3 - 1}{HGF^3 - (1 - \kappa)} \quad (1)$$

HGF represents the growth factor of aerosol particles due to water uptake under subsaturated conditions, which is the ratio between wet droplet diameter (D_{wet}) at a certain α_w , and dry particle diameter (D_{dry}). In this study, we follow the same approach as Li et al.³¹ to derive the HGF according to the COSMOtherm estimates, which considered the particles as a bulk phase while neglecting the size effect. Under the assumption of particle sphericity, HGF can be expressed by:

$$HGF = \left(\frac{D_{wet}}{D_{dry}} \right) = \left(\frac{V_{wet}}{V_{dry}} \right)^{\frac{1}{3}} \quad (2)$$

where V_{wet} is the wet droplet volume, and V_{dry} is the dry particle volume. Assuming volume additivity, HGF can be expressed using the volumes of solute (V_s) and water (V_{H_2O}).

$$HGF = \left(\frac{V_s + V_{H_2O}}{V_s} \right)^{\frac{1}{3}} = \left(1 + \frac{V_{H_2O}}{V_s} \right)^{\frac{1}{3}} \quad (3)$$

For each component j , its volume can be written using its mass at a certain α_w (m_j) and density (ρ_j):

$$V_j = \frac{m_j}{\rho_j} \quad (4)$$

As ρ_j is estimated under the assumption of close packing in COSMOtherm, the intermolecular hydrogen bond formation is not considered in the calculation of ρ_j .

By combining Eqs. (3) and (4), HGF can be further expressed as:

$$HGF = \left(1 + \frac{m_{H_2O} \cdot \rho_s}{m_s \cdot \rho_{H_2O}} \right)^{\frac{1}{3}} \quad (5)$$

where the mass ratios of m_{H_2O} to m_s can be predicted using the COSMOtherm-derived mass fraction of water at a certain α_w .

Using Eq. (5) to replace HGF in Eq. (1), we can express κ at a certain α_w as follows:

$$\kappa = \frac{m_{H_2O} \cdot \rho_s}{m_s \cdot \rho_{H_2O}} \cdot \left(\frac{1}{\alpha_w} - 1 \right) \quad (6)$$

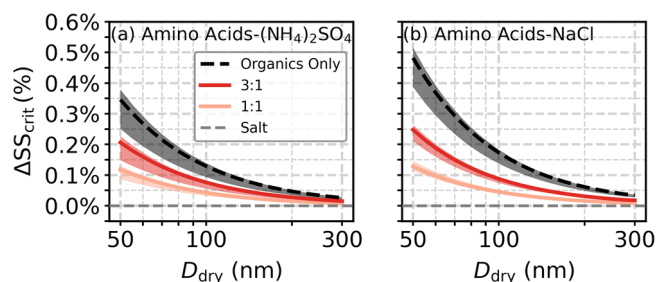


Fig. 4 | Comparison in critical supersaturation (SS_{crit}) between pure amino acid particles, amino acid particles and amino acid-salt mixture particles. Median values (lines) and interquartile ranges (shaded areas) of the difference in critical supersaturation (ΔSS_{crit}) between the pure amino acid particles (black dashed lines), amino acid-salt mixture particles at mass ratios of 3:1 (red solid lines) and 1:1 (orange solid lines) and pure inorganic salt particles (i.e., $(NH_4)_2SO_4$ or NaCl; grey dashed lines) over a range of dry particle size diameter (D_{dry}).

Modeling cloud droplet activation

The vapor pressure over a liquid surface can be derived using Köhler theory⁴⁶ as follows:

$$SS = \alpha_w \cdot \exp\left(\frac{4\sigma \cdot v_{H_2O}}{D_{wet} \cdot R \cdot T}\right) - 1 \quad (7)$$

where SS is the equilibrium supersaturation ratio of water over a droplet surface, σ is the surface tension of the droplet, v_{H_2O} is the molar volume of water, D_{wet} is the wet diameter, R is the universal gas constant (i.e., $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and the T is the temperature (i.e., 295 K in this study). The α_w term describes the solute effect (Raoult effect), and the geometric term $\exp\left(\frac{4\sigma \cdot v_{H_2O}}{D_{wet} \cdot R \cdot T}\right)$ (Kelvin term) describes how the interfacial curvature modifies the equilibrium vapor pressure.

Typically, σ is assumed to be equivalent to that of pure water (i.e., 72 mN m^{-1}). This simplification holds true only if the solutes present in the droplet are weakly surface-active. In this study, it is reasonable to approximate σ of the droplet as that of pure water since the adsorption isotherms for aqueous solutions of amino acids remain more or less the same as pure water⁴².

Using the COSMOtherm-derived α_w , we derive the values of SS across a set of D_{wet} of the droplet, and then identify the critical supersaturation (SS_{crit}) at which the derived SS reaches its maximum over D_{wet} . For surface-active aerosol constituents, the lower surface tension would decrease the SS_{crit} and increase the CCN activity of the aerosol particles, compared to aerosol particles containing only weakly surface-active constituents.

Data availability

All relevant data supporting the findings of this study are available via QUT Research Data Finder at https://doi.org/10.25912/RDF_1762770106961.

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Author contributions

Z.L. and N.H. conceived the study. Z.L. performed the data collection and hygroscopicity calculation. S.I. and N.H. performed the COSMOtherm calculations. Z.L. wrote the paper with contributions from all co-authors.

Competing interests

Dr Zijun Li is an Editorial Board Member for Communications Earth and Environment, but was not involved in the editorial review of, or the decision to publish this article. The authors also have no other competing interests to declare.

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