

Article

Thermodynamic Impact of Mineral Surfaces on Amino Acid Polymerization: Aspartate Dimerization on Ferrihydrite, Anatase and γ -alumina

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Abstract: The ubiquity of amino acids in carbonaceous meteorites has suggested that amino acids are widespread in our solar system, serving as a common class of components for the chemical evolution of life. However, there are a limited number of parameters for modeling amino acid polymerization at mineral–water interfaces, although the interfacial conditions inevitably exist on astronomical bodies with surface liquid water. Here, we present a set of extended triple-layer model parameters for aspartate (Asp) and aspartyl-aspartate (AspAsp) adsorptions on ferrihydrite, anatase, and γ -alumina determined based on the experimental adsorption data. By combining the parameters with the reported thermodynamic constants for amino acid polymerization in water, we computationally demonstrate how these minerals impact the AspAsp/Asp equilibrium over a wide range of environmental conditions. It was predicted, for example, that ferrihydrite strongly promotes Asp dimerization, leading to the AspAsp/Asp ratio in the adsorbed state up to 41% even from a low Asp concentration (0.1 mM) at pH 4, which is approximately 5×10^7 times higher than that attainable without mineral ($8.5 \times 10^{-6}\%$). Our exemplified approach enables us to screen wide environmental settings for abiotic peptide synthesis from a thermodynamic perspective, thereby narrowing down the geochemical situations to be explored for life's origin on Earth and Earth-like habitable bodies.

Keywords: adsorption; astrobiology; chemical evolution; origin of life; polymerization; surface complexation modeling

1. Introduction

Following the discoveries of thousands of exoplanetary systems [1,2], a significant effort is being devoted to the laboratory simulation of the formation and oligomerization of biologically relevant compounds on a planetary surface, thereby evaluating the possibility and architecture of life to exist [3–5]. Amino acids are frequently targeted compounds for several reasons: (1) they are major building blocks for Earth's life, (2) they have been synthesized in numerous experiments simulating primordial geochemical events [6], (3) they are representative soluble organic matter in extraterrestrial materials (carbonaceous chondrites and comets) [7,8], and (4) they facilitate various organic/inorganic reactions possibly crucial to life's origin [9,10]. Thus, the availability and versatility in prebiotic chemistry not limited to Earth suggest that amino acids are a major class of components for the extraterrestrial as well as the terrestrial origins of life.

At the mineral–water interface, amino acids exhibit considerably different polymerization reactivities from those in aqueous solution [11]. Although this phenomenon has long been studied in the prebiotic chemistry context, its parameterization for geo- and astro-chemical modeling applications remains limited. A limitation of this parameterization is the kinetic difficulty in

controlling the amino acid polymerization rate within experimentally monitorable level while suppressing other undesirable reactions. To accelerate the polymerization, experiments have typically been conducted at elevated temperatures (e.g., 200°C) with high concentrations of amino acids (e.g., 100 mM) [12]. However, the extrapolation of the results to those at naturally prevalent conditions, 0–50 °C for the early Archean ocean [13], is always difficult owing to the occurrence of side reactions (e.g., decomposition) and the kinetic complexity of mineral–water–solute interactions [14].

Thermodynamics provides a way to circumvent this problem. The equilibrium constant for amino acid polymerization on a mineral is expressed by combining the surface adsorption constants of the amino acid and its peptide with the polymerization constant in water (Figure 1a). Amino acids and peptides readily attain adsorption equilibria at ambient temperature, and the thermodynamic data of these dissolved species are available in the literature [15–17]. Thus, by experimentally obtaining the adsorption data as a function of reaction conditions and formulating a surface complexation model based on the results, the thermodynamically attainable peptide concentration on the mineral is computable over a wide range of environmental conditions.

We recently applied this methodology to L-aspartate (Asp)–goethite and L-lysine (Lys)–amorphous-silica systems [18,19]. In both systems, the adsorption was largely controlled by the electrostatic amino acid–surface interaction, resulting in the prediction that goethite promotes Asp dimerization at slightly acidic pH (4–5), while amorphous silica promotes Lys dimerization at slightly alkaline pH (~9). Since the goethite–Asp (or AspAsp) binding, which involved outer- and inner-sphere complexes [19], was stronger than the outer-sphere amorphous-silica–Lys (or LysLys) binding [18,20], the former system exhibited a greater increase in equilibrium dipeptide concentration, up to ~10⁵-fold enhancement of 0.1 mM Asp dimerization by 10 m² L⁻¹ goethite. Importantly, in the absence of minerals, Asp and Lys have similar pH dependence of dipeptide concentration at equilibrium [21]. Thus, our calculation indicated that the mineral–water interfacial condition is a crucial factor for the sequence and yield of the peptides producible abiotically.

In this study, we aim to expand the computable mineral–amino acid combinations for screening wider and diverse environmental settings for abiotic peptide formation. Given the promising role of goethite in Asp dimerization introduced above [19], we examined the influence of ferrihydrite, anatase, and γ-alumina on the AspAsp/Asp equilibrium. Ferrihydrite is a low-crystalline iron oxide precursor of goethite and hematite [22] possibly widespread even on the anoxic primordial Earth owing to the photochemical oxidation of siderite to Fe(III) minerals [23]. Anatase and γ-alumina are oxides of titanium and aluminum, respectively, which are common metal components on the Earth's crust. Although silica is also prevalent on the Earth surface, no adsorption of Asp and AspAsp was observed (data not shown), indicating the negligible influence of silica on Asp dimerization

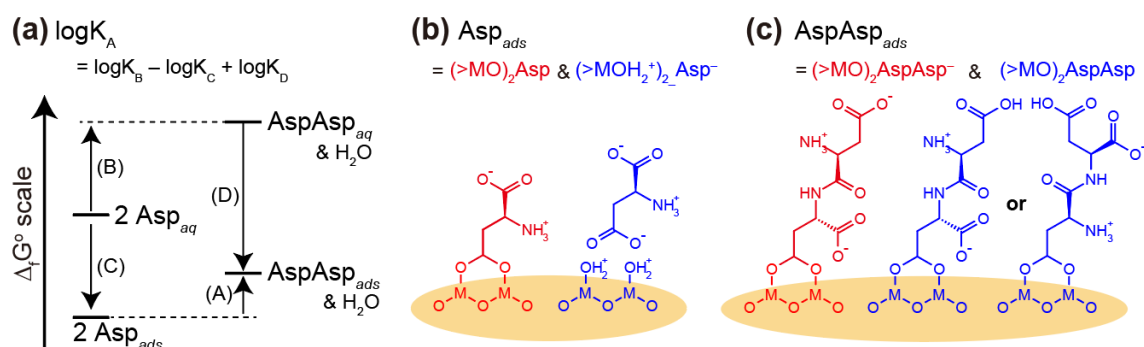


Figure 1. (a) Schematic showing the thermodynamic relationships among (A) the dimerization of adsorbed Asp (Asp_{ads}), (B) dimerization of dissolved Asp (Asp_{aq}), (C) adsorption of Asp_{aq} , and (D) adsorption of AspAsp_{aq} . The Asp and AspAsp surface species assumed in this study are depicted in (b) and (c), respectively.

thermodynamics. It should be noted that there are numerous experimental data for amino acid and

peptide adsorption in the literature. However, in many cases particularly for peptides, their reaction condition dependencies are not examined sufficiently for modeling amino acid polymerization in a wide range of environmental conditions (e.g., as a function of pH, electrolyte concentrations, amino acid concentration, and the solid/water ratio). To the best of our knowledge, the thermodynamic datasets available for such purposes are given by our previous studies alone [18,19].

2. Materials and Methods

2.1. Materials

Asp and AspAsp were purchased from Peptide Institute (Catalog No. 2704) and BACHEM (Catalog No. G-1565), respectively. Anatase was obtained from EM Japan (Catalog No.: NP-TIO2-4; $49.4 \text{ m}^2 \text{ g}^{-1}$; 99.98% purity [24]). γ -alumina was provided by Sumitomo Chemical (Catalog No.: AKP-G15; $164 \text{ m}^2 \text{ g}^{-1}$; $\geq 99.99\%$ purity). Ferrihydrite was prepared following a previously reported procedure [25,26]. To FeCl_3 aqueous solution (typically 10 mM), 0.1 or 1 M NaOH was added in a dropwise manner until the pH reached 8.0 in a glove box filled with N_2 gas ($>99.99995\%$ purity) at room temperature ($25^\circ\text{C} \pm 2^\circ\text{C}$). The resultant suspension was aged over 3 h under vigorous stirring at pH 8.0, and it was diluted to certain concentrations for use in adsorption experiments. The specific surface area of ferrihydrite was assumed to be $600 \text{ m}^2 \text{ g}^{-1}$ [25,26], and the solid/water ratio was calculated using the reported ferrihydrite chemical formula of $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ [27]. Milli-Q water (18.2 megohms) was used as the solvent for all the aqueous solutions. pH and temperature were monitored with a portable pH meter (Seven2Go Pro; Mettler Toledo).

2.2. Adsorption experiments

All adsorption experiments were conducted in a glove box filled with N_2 gas at $25^\circ\text{C} \pm 2^\circ\text{C}$. The initial Asp and AspAsp concentrations were set to 0.1 or 0.5 mM, and 10 or 100 mM NaCl was used as the background electrolyte. The solid/water ratios were 2.5 or 5 g L^{-1} for anatase and γ -alumina, and 0.136 or 0.27 g L^{-1} for ferrihydrite. The pH of the anatase and ferrihydrite suspensions was adjusted between 3 and 10 with reagent grade HCl or NaOH, whereas the pH range was limited to 5–10 for γ -alumina because of the rapid dissolution at acidic pH [28]. All the sample suspensions (4 mL for each) were prepared in a 15 mL polypropylene centrifuge tube and rotated at 25 rpm for 20 h to adequately attain the adsorption equilibria. Afterward, the samples were measured for pH, centrifuged at 8000 rpm for 10 min, and filtered with a polytetrafluoroethylene membrane filter.

The Asp and AspAsp remaining in the filtrates were quantified by a high-performance liquid chromatograph equipped with a postcolumn derivatization system with o-phthalaldehyde (JASCO HPLC system). A fluorescence detector was operated at 345 nm and 455 nm for excitation and emission, respectively. Five citrate buffer solutions with different citrate concentrations and pH were used as eluents in a stepwise manner. A cation-exchange column (AAPak Na II-S2; JASCO) was used at 50°C . To ensure reproducibility, we performed multiple independent runs under several sets of reaction conditions. The differences among the data obtained under identical conditions were less than 10%.

In the AspAsp samples, small amounts of Asp were observed because of the peptide-bond hydrolysis during the adsorption experiment. In most cases, the Asp concentrations were less than 0.5% of the initial AspAsp concentration, but relatively high values up to 1.5% were measured particularly when a high solid/AspAsp ratio was examined (e.g., 5 g L^{-1} anatase mixed with 0.1 mM AspAsp). AspAsp hydrolysis could be greater than those expected from the quantified Asp concentrations because of Asp adsorption. However, we did not consider the hydrolysis in the data analysis described below because the resultant overestimations of AspAsp adsorption were likely still insignificant compared to the uncertainties arising from the experimental reproducibility.

2.3. Thermodynamic calculation

All computations were performed with the extended triple-layer model (ETLM), a triple-layer model that consider the electrostatics of water dipole desorption during the ligand exchange reaction

[29,30]. ETLM differs from TLM only in the electrostatic term associated with inner-sphere adsorption, and it involves no additional fitting parameters. Thus, ETLM can be used in any geochemical modeling programs including TLM, such as GEOSURF [31], MINTEQL+ [32], PHREEQC [33], and visual-MINTEQ [34]. In this study, we used visual-MINTEQ. The protonation constants of Asp and AspAsp were set to the values reported in the NIST database [35] and literature [36], respectively (Table A1). The dissociation constants of dissolved NaOH, NaCl, and HCl were taken from [37], [38], and [39], respectively. The aqueous complexes between organic species and inorganic ions were not considered because of the lack of thermodynamic parameters for AspAsp. The mole fraction of the Asp forming complex with Na⁺ (Asp²⁻ + Na⁺ → Asp²⁻Na⁺), which is calculable with the reported constant (logK= 0.08 [35]), is at most 5% in the examined aqueous condition. This small fraction had no appreciable influence on the ETLM regression calculation of the experimental adsorption data (data not shown). The same should be true for AspAsp.

3. Results and Discussion

3.1. ETLM analysis of the experimental adsorption data

The ETLM calculation for solute–surface interaction requires parameters for surface species and surface charge properties in an aqueous solution. Specifically, it requires the specific surface area (A_s), surface site density (N_s), inner- and outer-layer capacitances (C₁ and C₂; we here set C₁ = C₂ in all calculations [24]), surface protonation constants (K₁ and K₂), electrolyte adsorption constants (K_{Na+} and K_{Cl-}), and, in our case, Asp and AspAsp adsorption constants. We set the values of N_s, C₁ (= C₂), K₁, K₂, K_{Na+} and K_{Cl-} for ferrihydrite to those reported in ref. [26] (Tables 1 and A2). For γ-alumina, the values of N_s and C₁ (= C₂) were taken from ref. [29], and K₁, K₂, K_{Na+} and K_{Cl-} were estimated from the ETLM fitting of the γ-alumina surface charge data (Figure A1a). Similarly, the values of N_s and C₁ (= C₂) for anatase were obtained from refs. [40] and [29], respectively, and K₁, K₂, K_{Na+} and K_{Cl-} were estimated from the ETLM fitting of anatase surface charge data (Figure A1b).

The Asp and AspAsp adsorption constants should be determined with stoichiometries consistent with the actual surface binding modes. However, even Asp adsorption remains controversial in spectroscopic and computational investigations (Table A3). The proposed functional groups crucial for Asp binding on TiO₂, for example, includes the amino group (NH₃⁺ or NH₂) [41,42], side chain methylene group [43], and either or both of the α-COO⁻ and β-COO⁻ groups [44–48]. These disagreements probably indicate the difficulty in determining the Asp interfacial structure rather than reflect the difference in the examined TiO₂ surface environments [49].

Table 1. Stoichiometries, electrostatic factors and equilibrium constants for the solute–surface interactions on ferrihydrite, anatase and γ-alumina considered in this study.

Reaction	Ψ	logK ^{MF 1}		
		ferrihydrite	anatase	γ-Al ₂ O ₃
>MOH + H ⁺ → >MOH ₂ ⁺	ψ ₀	3.7	3.1	4.2
>MOH → >MO ⁻ + H ⁺	−ψ ₀	−12.1	−9.9	−12.3
>MOH + Na ⁺ → >MO ⁻ Na ⁺ + H ⁺	−ψ ₀ + ψ _B	−8.2	−7.1	−8.4
>MOH + Cl ⁻ + H ⁺ → >MOH ₂ ⁺ Cl ⁻ + H ⁺	ψ ₀ − ψ _B	8.1	5.9	7.9
2>MOH + Asp ²⁻ + 2H ⁺ → (>MO) ₂ Asp + 2H ₂ O	−	18.2	17.2	17.6
2>MOH + Asp ²⁻ + 3H ⁺ → (>MOH ₂ ⁺) ₂ Asp ⁻	2ψ ₀ − ψ _B	30.2	26.5	27.7
2>MOH + AspAsp ³⁻ + 2H ⁺ → (>MO) ₂ AspAsp ⁻ + 2H ₂ O	−ψ _B	21.2	19.0	19.5
2>MOH + AspAsp ³⁻ + 3H ⁺ → (>MO) ₂ AspAsp + 2H ₂ O	−	23.5	19.5	22.0

¹ The mole fraction-based equilibrium constants as inputs in Visual MINTEQ. See Appendix Table 3 presented by ref. [19] for the correlations among different thermodynamic expressions for the surface complexation reactions.

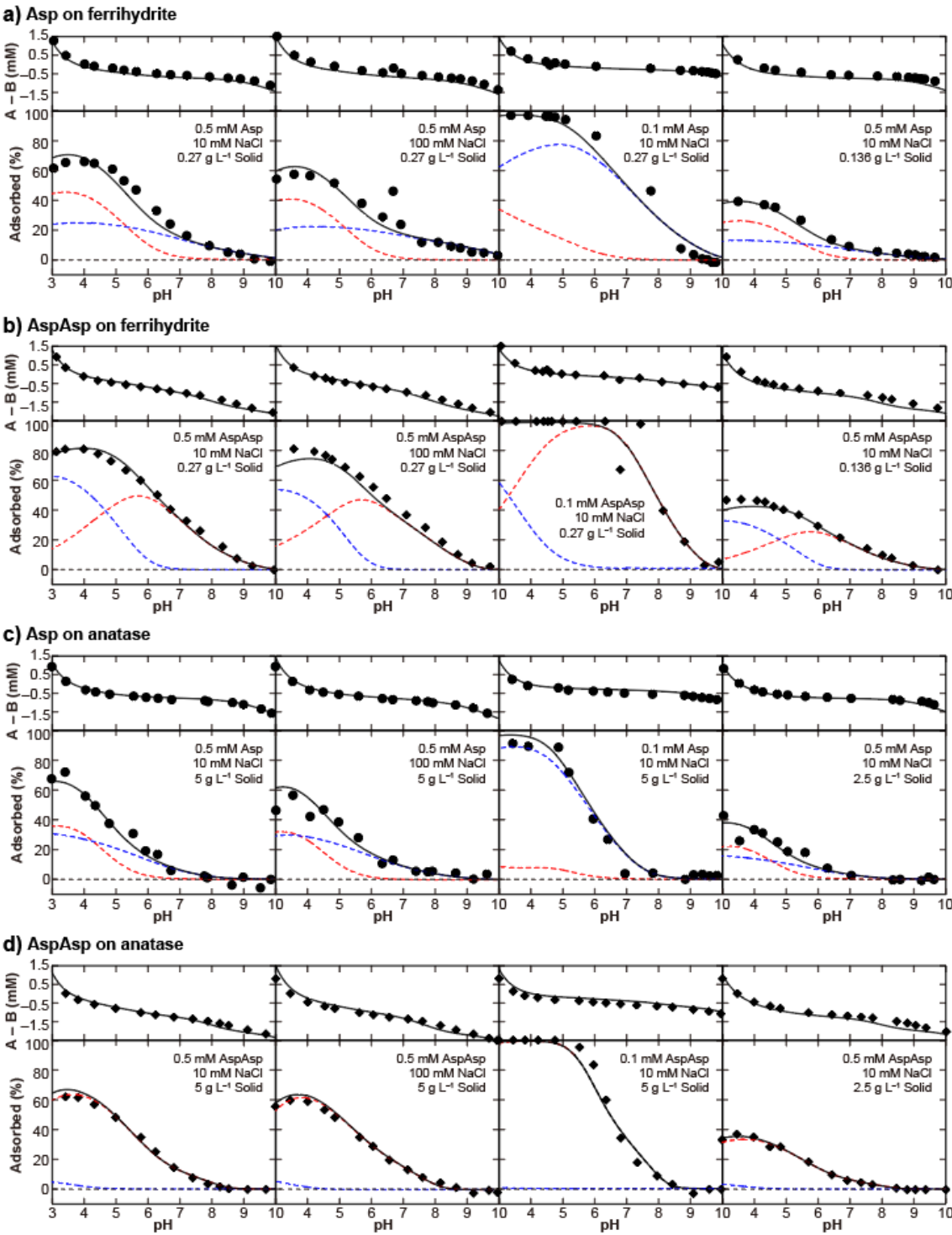


Figure 2. Percentages of the adsorbed Asp and AspAsp on ferrihydrite (a and b), anatase (c and d), and γ -alumina (e and f) at various pH, the initial Asp (or AspAsp) concentration, NaCl concentration, and solid/water ratio are shown in the bottom sections, and the responses of pH to the addition of an acid (A; HCl) or base (B; NaOH) into the sample suspensions are presented in the top sections. Symbols represent the experimental data, and solid lines are the regression fits with the ETLTM. Red and blue lines in the bottom sections show the contributions of the red- and blue-colored surface species depicted in Figure 1b and c to the total Asp or AspAsp adsorptions (black lines).

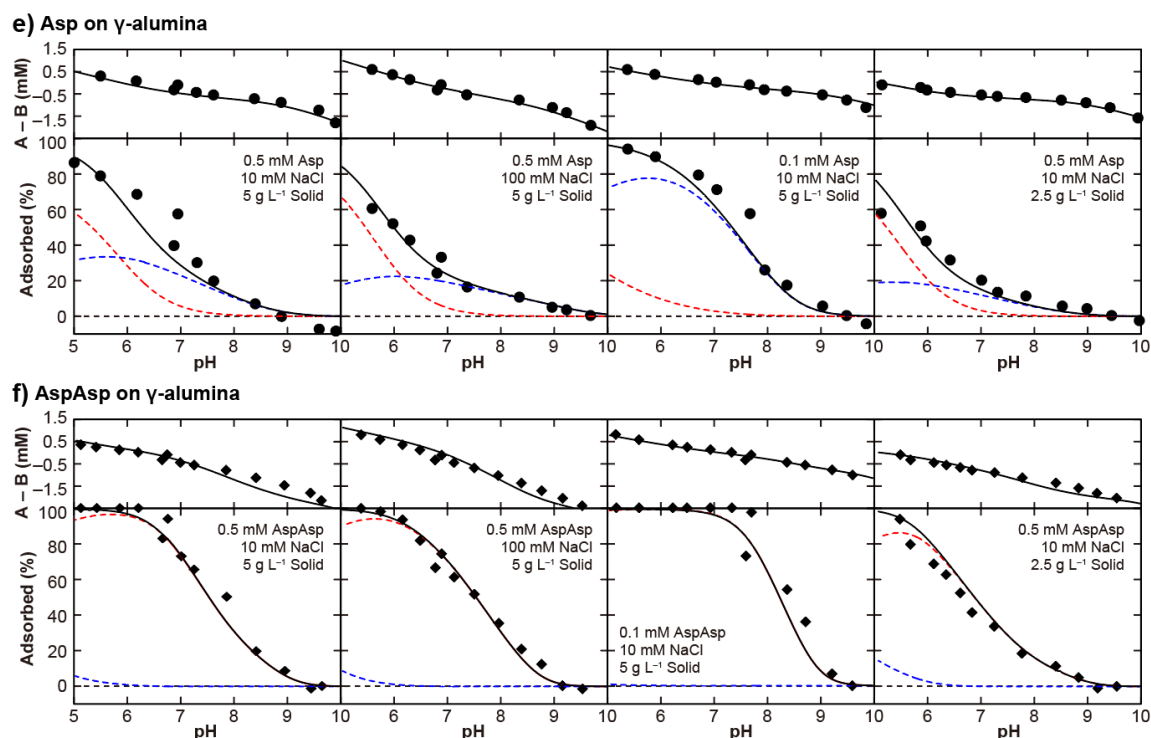
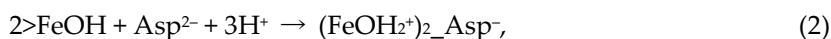


Figure 2. (Continued).

In our previous ETLM study for Asp adsorption on goethite [20], we assumed inner- and outer-sphere surface complexations using the β -COO⁻ group (Figure 1b):

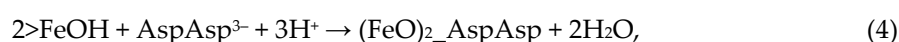


This model agreed with the following experimental observations: (1) the amount of Asp adsorption increased with the positive charge development on goethite by pH acidification, which indicates the electrostatic interaction to be an important factor; (2) no adsorption of glycine and glycylglycine occurred, which suggests a negligible contribution of the α -COO⁻ group to Asp adsorption; and (3) the same stoichiometries adequately represented AspGly adsorption, which supports Asp 'standing' geometry anchoring the β -COO⁻ group rather than Asp 'lying down' conformation on the goethite surface. Similar to goethite, ferrihydrite, γ -alumina, and anatase possess net positive surface charges in neutral to acidic pH [26] (Figure A1). Since the four minerals exhibited similar pH and electrolyte-concentration dependences of Asp adsorption that were attributable to the electrostatic Asp-surface interaction (Figure 2), we applied the stoichiometries in Equations (1) and (2) to all the ETLM fittings.

Our model is different from the ETLM description of Asp adsorption on rutile by Jonsson et al. [36], where the tetradentate-tetranuclear inner-sphere complex connecting the α - and β -COO⁻ groups with four surface Ti atoms was assumed, with an outer-sphere complex, following the ATR-IR observation by ref. [46]. However, as mentioned above, such strong α -COO⁻ group-surface binding is unlikely because of the proximity of the α -NH₃⁺ group. The IR absorption signals of the α - and β -COO⁻ groups of Asp are strongly overlapping, making the unambiguous identification of the respective chemical states difficult. Further, the spectral distortion associated with the ATR technique [50–52] complicates the data interpretation. Different interpretations for Asp binding mode on TiO₂ were proposed by ref. [46] and ref. [44] (Table A3), although their observed spectral profiles were similar to each other. From a modeling perspective, the adsorption data by Jonsson et al. [36] can be represented by Equations (1) and (2) (Figure A2a–d). Additionally, the two equations allow the simulation of the experimental data by ref. [41] for Asp adsorption on anatase (Figure A2e–g). In

contrast, the application of the four surface-sites occupancy model [36] to our results requires surface-site densities of up to 5.7, 2.0, and 4.2 nm⁻² on ferrihydrite, γ -alumina and anatase, respectively. The value for ferrihydrite is much larger than the ferrihydrite site density available for the multidentate-multinuclear complexes estimated by ref. [53] (2.8 ± 0.6 nm⁻²). Thus, although further investigations with advanced surface analytical techniques are required, we maintain our interpretation that Asp forms inner- and outer-sphere complexes on all the examined minerals via the β -COO⁻ group (Figure 1b). Our model adequately represented the experimental Asp adsorption data at various pH, the initial Asp concentration, NaCl concentration, and solid/water ratio (Figure 2a,c,e). Thus, the determined adsorption constants (Table 1) can be used to simulate the solid-liquid partitioning of Asp in a wide range of environmental conditions, from which the thermodynamic property of adsorbed Asp is calculable relative to the property of the dissolved counterpart (Figure 1a).

Similarly, for AspAsp, we applied the stoichiometries previously used for AspAsp adsorption on goethite [19] (Figure 1c):



Good ETLM fits were achieved in all the examined reaction conditions (Figure 2b,d,f).

3.2. Thermodynamic prediction of Asp dimerization at the mineral–water interface

Asp is one of the oldest biological components among the 20 coded protein amino acids [54–56]. Since numerous nonenzymatic processes are known to generate Asp [6], abiotically formed Asp is likely to have distributed widely on the primitive Earth, being transported through water circulation to various mineral–water interfaces. The same situation may be expected on Earth-like habitable bodies given the ubiquity of Asp in carbonaceous chondrites [57].

To evaluate the Asp dimerization reactivity under interfacial conditions from a thermodynamic perspective, we computed the monomer–dimer equilibria of Asp on ferrihydrite, γ -alumina, and anatase with the ETLM parameters obtained in this study. The formation constants from Asp²⁻ of all the dissolved and adsorbed AspAsp species were calculated by setting the logK value for the zwitterionic Asp dimerization in water (i.e., Asp[±] + Asp[±] → AspAsp[±] + H₂O) to –3.0 [15] and by combining this value with the respective AspAsp protonation and adsorption constants (Table A4). The examined pH and NaCl concentrations were 3–10 (5–10 for γ -alumina) and 1–100 mM, respectively, corresponding to a range of natural waters in rivers, soil, terrestrial springs, saline lakes, and rainfall [58–62]. There is no definitive constraint on the α -amino acid abundance in primitive

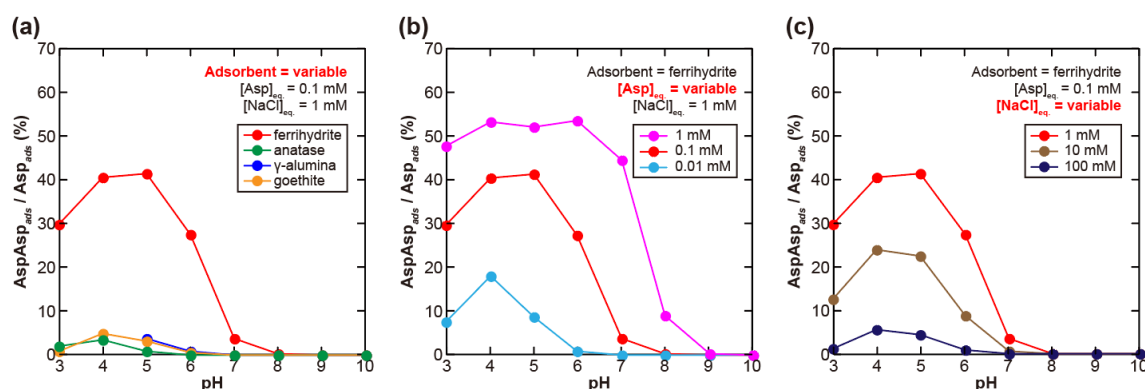


Figure 3. Thermodynamic prediction of the AspAsp/Asp molecular ratio in the adsorbed state. In (a), the ratio is calculated for the case of various mineral adsorbents at fixed equilibrium Asp and NaCl concentrations (0.1 and 1 mM, respectively), whereas the influences of the equilibrium Asp and NaCl concentrations are presented only for ferrihydrite in (b) and (c). Note that the results are independent on the solid/water ratio in the ‘open’ system examined here.

environments. Thus, the Asp concentration was arbitrarily set to 0.01, 0.1, or 1 mM to assess the influence of this parameter on the AspAsp/Asp equilibrium.

When no external Asp supply is assumed, the Asp concentration in the interfacial water decreases through Asp adsorption and dimerization, whereas the Asp concentration is maintained if a sustained flow of Asp-containing fluid is considered. Although both the 'closed' and 'open' systems are likely to exist in nature, we consider the latter case because calculations with fixed aqueous species concentrations give the mole fractions of the adsorbed species (and hence, the AspAsp/Asp ratio in the adsorbed state) independent of the amount and specific surface area of the mineral. Thus, the open system is beneficial for directly comparing the thermodynamic impacts per certain surface area of different minerals. In other words, this assumption can 'normalize' the availabilities of mineral surfaces that vary with environmental situations. In all the dimerization calculations described below, AspAsp was computed to be mostly adsorbing (>99.9%) unless the Asp-to-AspAsp conversion ratio was less than 0.1%. Thus, the formation and accumulation of AspAsp are expected to occur only on the surface under a continuous Asp supply from an aqueous solution. Notice that the thermodynamic calculation is applicable to various environmental simulations. Owing to space limitations, we present some representative results in the parameter range specified above, and discuss the feasibility of abiotic Asp dimerization at the mineral–water interface.

Figure 3a shows the AspAsp/Asp ratios on ferrihydrite, γ -alumina, anatase, and goethite equilibrated with 0.1 mM Asp in 1 mM NaCl solution. Ferrihydrite exhibited the strongest enhancement in the neutral to acidic pH region, leading to an AspAsp/Asp ratio up to 41%, which was approximately 5×10^7 times higher than that attainable without mineral ($8.5 \times 10^{-6}\%$ at pH 4). Larger percentages of up to 53% were computed from 1 mM Asp (Figure 3b), while higher NaCl concentrations suppressed the reaction (Figure 3c). Factors influencing the AspAsp/Asp ratio include the Asp concentration and AspAsp stability relative to Asp in the adsorbed state. Ferrihydrite adsorbed Asp and AspAsp with the highest surface densities among the four minerals (Figure A3a and d) and adsorbed AspAsp with a greater affinity than Asp (Figure A3). These surface properties make ferrihydrite the most effective promoter of Asp dimerization. Specifically, in equilibrium with 0.1 mM Asp in 1 mM NaCl at pH 4, 1.25 Asp molecules per square nanometer of ferrihydrite were calculated (Figure 3b; the Asp-to-AspAsp conversion was not considered in this calculation). Taking a typical distance from a solid surface to the β -plane (5 Å [63]) into account, the Asp surface density corresponds to the interfacial concentration of 4.2 mol L^{-1} , which is 4.2×10^4 times larger than the bulk Asp concentration (0.1 mM). Thus, the Asp concentration factor gives a 1.7×10^9 times enhancement of the equilibrium AspAsp/Asp ratio. Again, this simple calculation does not consider the adsorptive competition between Asp and AspAsp.

A drawback of ferrihydrite is its instability in water. In nature, ferrihydrite occurs in the early stage of weathering and gradually transforms into more stable forms, such as goethite and hematite, with reduced surface areas and lower adsorptivities [64]. Therefore, for the surface to promote Asp dimerization, the addition of crystallization inhibitors (e.g., silicate [65]) and/or improvement of the surface catalytic activity (e.g., doping of metals with different valence states) may be necessary. In our Asp adsorption experiments with ferrihydrite, no AspAsp was observed (detection limit: $\sim 0.001 \text{ mM}$) even after the basification of the sample suspensions to release adsorbed species.

Nonetheless, its excellent adsorptivity for AspAsp should have been advantageous for prebiotic Asp polymerization. Numerous abiotic mechanisms are known to polymerize amino acids [66–69]. Ferrihydrite likely trapped and concentrated the resultant AspAsp even from a dilute aqueous solution. If a ferrihydrite-coated sandstone with 10% porosity, which corresponds to the pore volume to mass ratio of 0.042 L kg^{-1} [70], is considered, 0.1 wt% of ferrihydrite enables the accumulation of 1.4 mmol AspAsp per one-kilogram of sandstone from a 0.01 mM AspAsp-containing solution at pH 4 (background electrolyte: 1 mM NaCl). The accumulated AspAsp will eventually be released through the aging of ferrihydrite, but its transportation with limited diffusion onto a catalytic surface may lead to the next stage of peptide bonding. AspAsp desorption is also caused by raising the pH and NaCl concentration (Figure 3a–c). Conversely, a pH increase induces ferrihydrite precipitation. Thus, the repeated cycles of Asp accumulation, desorption, and polymerization may have been possible through geochemical processes with fluctuating water flow, such as rainfall in dry

environments and water discharge from terrestrial vent systems [71]. In dry conditions, ferrihydrite and the other three minerals catalyze peptide bond formation [72–75]. Thus, Asp might also have polymerized on a single mineral surface through wetting-drying cycles.

In brine environments (e.g., saline lakes and sea), the adsorption-derived shift of the monomer-dimer equilibrium is limited (Figure 3c). However, because AspAsp adsorption is less dependent on NaCl concentration than Asp adsorption (Figure A3c and f), brine environments may be advantageous for selectively accumulating AspAsp from aqueous Asp-AspAsp mixtures. For ferrihydrite, for example, the adsorptive competition of an equimolar concentration of Asp and AspAsp (0.01 mM) results in a surface AspAsp/Asp ratio of 1.37 in the presence of 1 mM NaCl at pH 4 (Asp dimerization is not considered). The ratio increases to 1.54 when 100 mM NaCl is used as the background electrolyte. Thus, mineral surfaces can selectively capture AspAsp relative to Asp in both on-land and undersea settings, increasing the favorability of Asp peptide elongation.

4. Summary and future research directions

In this article, we demonstrated a thermodynamic approach to evaluate the impact of mineral surfaces on amino acid polymerization using ferrihydrite, anatase, and γ -alumina as the minerals for Asp adsorption and dimerization. This approach enables us to theoretically screen wide environmental settings, thereby narrowing down the parameter space to be examined in-depth (e.g., by laboratory simulations) for determining suitable geochemical situations for abiotic peptide synthesis. The obtained adsorption constants are useful not only for calculating the amino acid/peptide equilibria in the adsorbed state but also for simulating the selection and accumulation of the respective compounds from an aqueous solution.

An important next step is determining the key interfacial mechanisms controlling Asp and AspAsp adsorptions, thereby enabling the prediction of the adsorption constants for any mineral–Asp (or AspAsp) combinations based on a limited number of known constants. There is a predictive scheme for simple inorganic ions (e.g., Na^+ and Cl^-) [29,76], but its application to our results did not provide a theoretically explainable outcome (data not shown), possibly because of the presence of several functional groups in Asp and AspAsp structures. Our computational results are, in some cases, not immediately understandable; for example, denser AspAsp adsorption was calculated on goethite than on anatase under the same reaction conditions (Figure A3d) while the opposite relationship was obtained for that of Asp (Figure A3a). Because there are tendencies that anatase dehydrates chemisorbed molecules whereas adsorbates on goethite retain their solvation shells [63], functional groups not directly involved in AspAsp adsorption (e.g., $-\text{NH}_3^+$ group) might have a stronger influence on the net binding strength on anatase than that on goethite. For the AspAsp–anatase system, in fact, the contribution of the net-neutral surface species ($(>\text{MO})_2\text{AspAsp}$) was calculated to be minor relative to the negatively charged species ($(>\text{MO})_2\text{AspAsp}^-$) (Figure 2f), which was a cause of the relatively low affinity of anatase for AspAsp adsorption (Figure A3a). The role of each functional group should be elucidated to clarify AspAsp–surface interactions. A survey of sulfide minerals is also meaningful because sulfide-rich hydrothermal vent environments are among the most plausible settings for life's origin on Earth, and possibly so on Earth-like habitable bodies [77–83]. Further experimental and theoretical investigations on the topics mentioned above will lead to a better understanding of the suitable mineral–water interfacial conditions for abiotic peptide synthesis crucial for the emergence of life.

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Appendix A

Table A1. Protonation constants of Asp [35] and AspAsp [36].

Reaction	logK	Reaction	logK
$\text{Asp}^{2-} + \text{H}^+ \rightarrow \text{Asp}^-$	9.66	$\text{AspAsp}^{3-} + \text{H}^+ \rightarrow \text{AspAsp}^{2-}$	8.11
$\text{Asp}^{2-} + 2\text{H}^+ \rightarrow \text{Asp}^{\pm}$	13.37	$\text{AspAsp}^{3-} + 2\text{H}^+ \rightarrow \text{AspAsp}^-$	12.50
$\text{Asp}^{2-} + 3\text{H}^+ \rightarrow \text{Asp}^+$	15.32	$\text{AspAsp}^{3-} + 3\text{H}^+ \rightarrow \text{AspAsp}^{\pm}$	15.87
		$\text{AspAsp}^{3-} + 4\text{H}^+ \rightarrow \text{AspAsp}^+$	18.45

Table A2. The specific surface area (A_s), the surface site density (N_s), solid concentration (C_s), and inner- and outer-layer capacitances (C_1 and C_2) of ferrihydrite, anatase and γ -alumina.

Oxide	A_s ($\text{m}^2 \text{g}^{-1}$)	N_s (nm^{-1})	C_s (g L^{-1})	$C_1 = C_2$ ($\mu\text{F cm}^{-1}$)
Ferrihydrite	600	3.8	0.136 or 0.27	130
anatase	164	3	2.5 or 5	131
γ -alumina	49.4	8	2.5 or 5	99

Table A3. Summary of the reported spectroscopic and computational interpretations of the Asp binding structure on oxide minerals.

Oxide	Method ¹	Asp	pH	Electrolyte	Asp adsorption mode ²	Ref.
goethite	ATR-IR & DFT	1, 5, or 10 mM	3, 6, or 11	0.01, 0.1, or 0.2 M NaCl	At pH 3: The BB ISC binding the α - and γ -COO ⁻ groups with two surface Fe atoms At pH 6: Primarily an OSC with a minor contribution of the IS complex as observed at pH 3 At pH 11: The HB between the NH ₂ group and surface hydroxyl groups	[84]
magnetite	MD	0.5 mM	3.5	0.1 M NaCl	The electrostatic interaction involving monodentate α -COO ⁻ -Fe and γ -COO ⁻ -Fe bindings and a tridentate NH ₃ ⁺ -O binding.	[85]
γ -Al ₂ O ₃	ATR-IR	3 or 7 mM	2.8, 3.8, or 6.0	0.1 M NaCl	The BB ISC binding the γ -COO ⁻ group with two surface Al atoms and the TT ISC binding the α - and γ -COO ⁻ groups with four Al atoms	[86]
anatase	XPS	0.4, 1.2, or 1.5 $\mu\text{mol m}^{-2}$	4	–	An ISC involving the NH ₂ group	[41]
anatase	DFT	–	–	–	An OSC involving the side-chain CH ₂ group	[43]
anatase	MOPS	–	–	–	The HB between the NH ₃ ⁺ group and the surface oxygen	[42]
rutile	ATR-IR & QCC	0.1, 1, or 4.4 mM	3 or 6	0.1 M NaCl	An OSC involving the α - and γ -COO ⁻ groups	[44]
rutile	DFT	–	–	–	A complex involving the α -COO ⁻ and NH ₃ ⁺ groups (the binding mode (ISC or OSC) depends on the initial setting for water molecules)	[45]
TiO ₂	ATR-IR	0.3 mM	1.5–10.8	5 mM N(CH ₃) ₄ ClO ₄	The TT ISC binding the α - and γ -COO ⁻ groups with four surface Ti atoms	[46]
TiO ₂	SFG	0.1–5 mg ml ⁻¹	3	0.02 M NaCl	An ISC involving a monodentate COO ⁻ -Ti binding and a HB involving another COO ⁻ group	[47]
TiO ₂	NMR & MD	10 mM	7	20 mM phosphate	An OSC involving the α -COO ⁻ and NH ₃ ⁺ groups	[48]

¹Abbreviations: ATR-IR: attenuated total reflection infrared spectroscopy, DFT: density functional theory calculation, MD: molecular dynamics simulation, MOPS: modeling within the MOPS algorithm [87], QCC: quantum chemical calculation, SFG: sum frequency generation vibrational spectroscopy.

²Abbreviations: ISC: inner-sphere complex, OSC: outer-sphere complex, HB: hydrogen bonding, BB: bidentate-binuclear, TT: tetradentate-tetranuclear.

Table A4. Formation constants from Asp²⁻ of the dissolved and adsorbed AspAsp species used for the equilibrium calculation of Asp dimerization in the presence of minerals (Figure 3).

Reaction	logK			
	ferrihydrite	anatase	γ-Al ₂ O ₃	goethite ²
2Asp ²⁻ + H ⁺ → AspAsp ³⁻		7.9		
2Asp ²⁻ + 2H ⁺ → AspAsp ²⁻		16.0		
2Asp ²⁻ + 3H ⁺ → AspAsp ⁻		20.4		
2Asp ²⁻ + 4H ⁺ → AspAsp [±]		23.7		
2Asp ²⁻ + 5H ⁺ → AspAsp ⁺		26.3		
2>MOH + 2Asp ²⁻ + 3H ⁺ → (>MO) ₂ AspAsp ⁻ + 3H ₂ O	29.3 ¹	26.9 ¹	27.4 ¹	27.7 ¹
2>MOH + 2Asp ²⁻ + 4H ⁺ → (>MO) ₂ AspAsp + 3H ₂ O	31.4 ¹	27.4 ¹	29.9 ¹	31.9 ¹

¹ Mole fraction-based equilibrium constants. ² Taken from ref. [19].

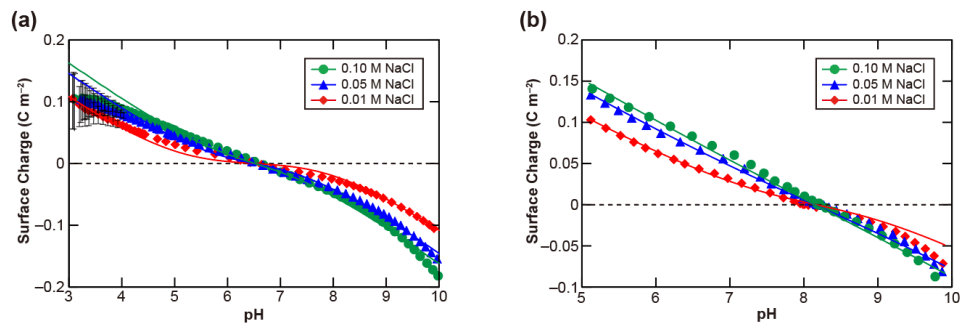


Figure A1. Surface charge densities of (a) anatase and (b) γ-alumina as a function of pH in 10, 50, and 100 mM NaCl. Symbols denote the experimental acid–base titration data, whereas solid lines represent the ETLM calculation with the parameters presented in Table 1.

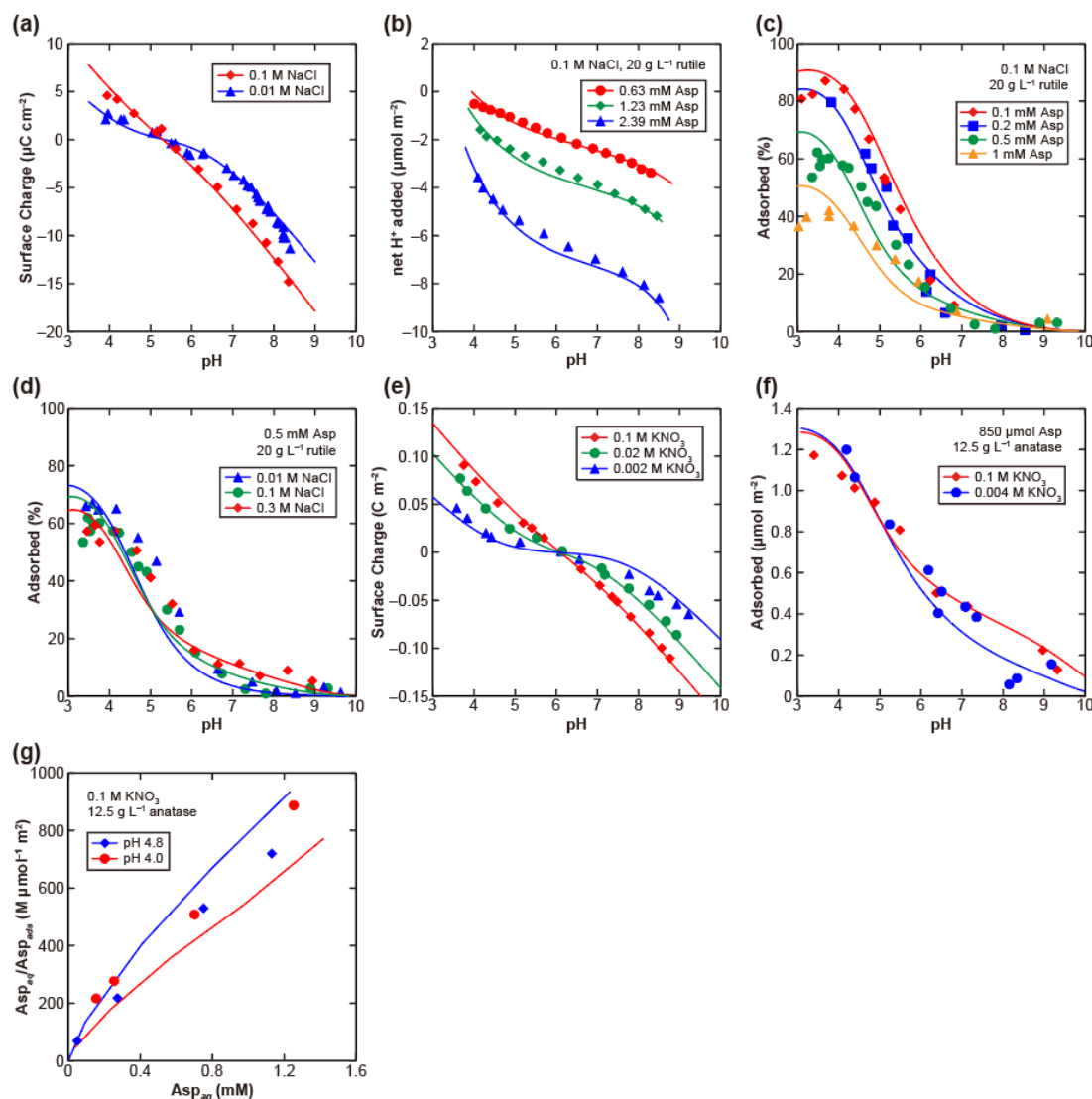


Figure A2. ETLM fittings (lines) of the reported experimental data (symbols) for Asp adsorption on rutile [40] (a–d) and on anatase [41] (e–g). The ETLM parameters used for these fittings are: $A_s = 18.1 \text{ m}^2 \text{ g}^{-1}$, $N_s = 3 \text{ nm}^{-2}$, $C_1 (= C_2) = 1.2 \text{ F m}^2$, $\log K_1 = 2.52$, $\log K_2 = -8.23$, $\log K_{\text{Na}^+} = -5.6$, $\log K_{\text{Cl}^-} = 5.0$, $\log K_{(\text{FeO})_2\text{Asp}} = 17.0$, and $\log K_{(\text{FeOH}_2)_2\text{Asp}^-} = 24.0$ for the Asp–rutile system, and $A_s = 47 \text{ m}^2 \text{ g}^{-1}$, $N_s = 3 \text{ nm}^{-2}$, $C_1 (= C_2) = 1.08 \text{ F m}^2$, $\log K_1 = 2.7$, $\log K_2 = -9.3$, $\log K_{\text{K}^+} = -6.4$, $\log K_{\text{NO}_3^-} = 5.8$, $\log K_{(\text{FeO})_2\text{Asp}} = 17.4$, and $\log K_{(\text{FeOH}_2)_2\text{Asp}^-} = 27.3$ for the Asp–anatase system. The values of N_s , $C_1 (= C_2)$, K_1 , K_2 , K_{Na^+} , and K_{Cl^-} for rutile were taken from ref. [40], and the values of $K_{(\text{FeO})_2\text{Asp}}$ and $K_{(\text{FeOH}_2)_2\text{Asp}^-}$ were determined by the ETLM fitting of the experimental Asp adsorption data (b–d). The values of N_s , $C_1 (= C_2)$, K_1 and K_2 for anatase were taken from ref. [29], and the values of K_{K^+} and $K_{\text{NO}_3^-}$ were estimated from the ETLM fitting of the anatase surface charge data (e). The values of $K_{(\text{FeO})_2\text{Asp}}$ and $K_{(\text{FeOH}_2)_2\text{Asp}^-}$ were then determined based on the Asp adsorption data (f,g). All $\log K$ values are presented as the mole fraction-based equilibrium constants.

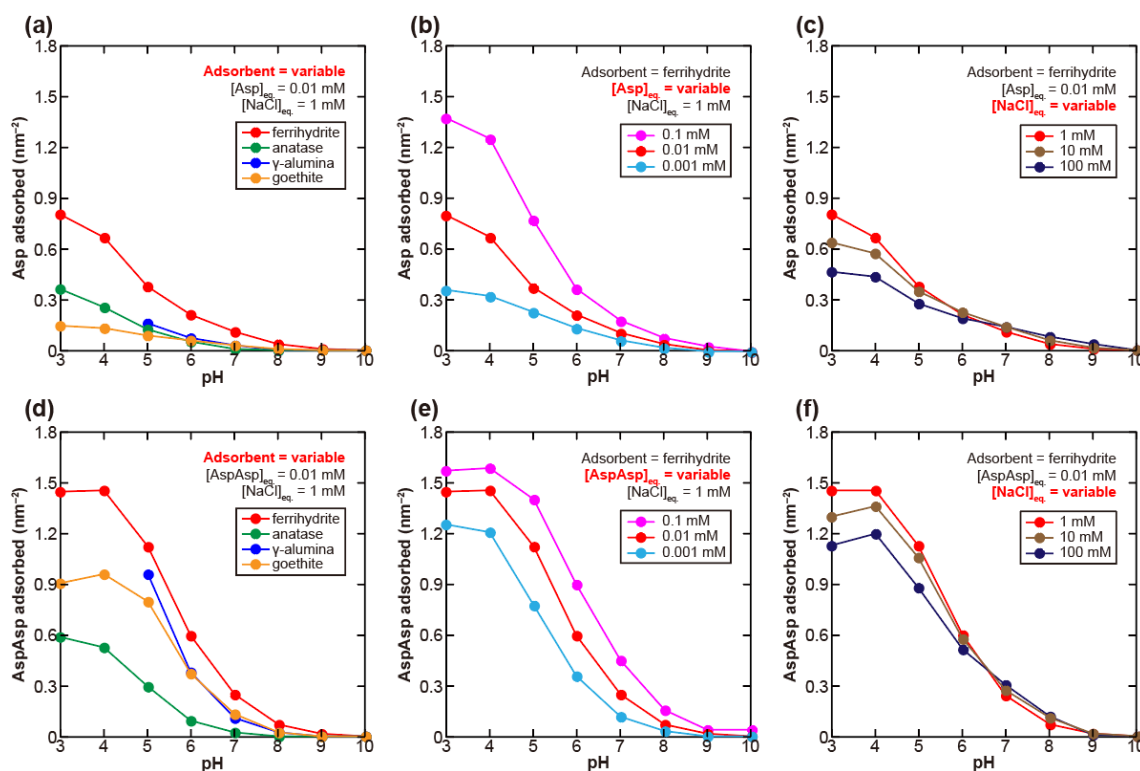


Figure A3. Thermodynamic prediction of the surface densities (the number of molecules per a square nanometer) of adsorbed Asp (a–c) and AspAsp (d–f). Interconversion between Asp and AspAsp is not considered in this calculation. In (a) and (d), the densities on various mineral adsorbents were calculated at fixed equilibrium Asp (or AspAsp) and NaCl concentrations (0.01 and 1 mM, respectively), whereas the influences of the equilibrium Asp (or AspAsp) and NaCl concentrations are presented only for ferrihydrite in (b), (c), (e), and (f). Note that the results are independent on the solid/water ratio in the ‘open’ system examined here.

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