

Amorphous Silica-Promoted Lysine Dimerization: a Thermodynamic Prediction

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Abstract It has long been suggested that mineral surfaces played a crucial role in the abiotic polymerization of amino acids that preceded the origin of life. Nevertheless, it remains unclear where the prebiotic process took place on the primitive Earth, because the amino acid–mineral interaction and its dependence on environmental conditions have yet to be understood adequately. Here we examined experimentally the adsorption of L-lysine (Lys) and its dimer (LysLys) on amorphous silica over a wide range of pH, ionic strength, adsorbate concentration, and the solid/water ratio, and determined the reaction stoichiometries and the equilibrium constants based on the extended triple-layer model (ETLM). The retrieved ETLM parameters were then used, in combination with the equilibrium constant for the peptide bond formation in bulk water, to calculate the Lys–LysLys equilibrium in the presence of amorphous silica under various aqueous conditions. Results showed that the silica surface favors Lys dimerization, and the influence varies greatly with changing environmental parameters. At slightly alkaline pH (pH 9) in the presence of a dilute NaCl (1 mM), the thermodynamically attainable LysLys from 0.1 mM Lys reached a concentration around 50 times larger than that calculated without silica. Because of the versatility of the ETLM, which has been applied to describe a wide variety of biomolecule–mineral interactions, future experiments with

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the reported methodology are expected to provide a significant constraint on the plausible geological settings for the condensation of monomers to polymers, and the subsequent chemical evolution of life.

Keywords Adsorption · Extended triple layer model · Origin of life · Surface complexation modeling

Introduction

It has long been suggested that mineral surfaces played a crucial role in the chemical evolution of life. The proposed functions beneficial to life's origin include the selection and concentration of key monomers from dilute aqueous solutions (Hazen et al. 2001; Baaske et al. 2007), the activation of the adsorbed monomers' polymerization to biopolymers (Ferris 2006; Kitadai et al. 2017), and the promotion of the emergence of biological functions such as replication and compartmentalization (Hanczyc et al. 2003; Wächtersäuser 2006). Thermodynamics is a quantitative technique to characterize the interface processes of adsorbed molecules. Using α -amino acids as representative constituents of prebiotic chemistry, a number of experimental and theoretical works have quantified the adsorption constants (K) and the adsorption Gibbs energies ($\Delta_r G_{ad}^o$) on various minerals (Lahav and Chang 1976; Rimola et al. 2013). When these parameters are available for peptides, their comparison with ones for amino acids allows for evaluation of the effect of mineral surfaces on the monomer–polymer equilibria. Basiuk and co-workers estimated the $\Delta_r G_{ad}^o$ for glycine (Gly) and glycine polymers (Gly₂–Gly₄) on amorphous silica by a chromatographic retention measurement at 19–21 °C and neutral pH (Basiuk et al. 1995). They showed that the values of $\Delta_r G_{ad}^o$ shift negatively with increasing peptide length, hence the silica surface has a positive influence on Gly polymerization. A similar conclusion has been made for the Gly–montmorillonite system, where the $\Delta_r G_{ad}^o$ values were obtained from the adsorption isotherm data at 25 °C and neutral or slightly acidic pH (Greenland et al. 1965; Kalra et al. 2003). Nevertheless, it remains unclear whether these minerals promote amino acid polymerization in natural environments, because the experimentally determined adsorption data are only useful at the same condition as the examined ones. For a better understanding of the minerals' effects on the primitive Earth with various geological settings, adsorption data needs to be obtained in a wide range of environmental conditions (pH, ionic strength, adsorbate concentration, the mineral/water ratio, etc.), and be integrated into a theoretical model that can describe the adsorption as a function of the variables.

Here, we report a thermodynamic prediction for L-lysine (Lys) dimerization on amorphous silica as the first example of this approach. The extended triple layer model (ETLM) (Sverjensky 2005; Sverjensky and Fukushi 2006) was used for the surface complexation modeling because it enables us to characterize amino acid adsorption with regard to the solid/liquid distribution, surface speciation, and their dependences on environmental conditions with spectroscopically and theoretically consistent trends (Sverjensky et al. 2008; Jonsson et al. 2010; Parikh et al. 2011). Lys was chosen because its abiotic formation has been demonstrated experimentally under simulated prebiotic conditions (Plankensteiner et al. 2006; Marshall 1994; Singh et al. 2015). It has been argued that Lys is a relatively later

biological invention among 20 coded protein amino acids (Trifonov 2000; Higgs and Pudritz 2009; van der Gulik et al. 2009). However, considering its importance in many enzymatic processes (Voet and Voet 2011), it would be safe to say that the prebiotically formed Lys could facilitated the origin and early evolution of life. The Lys–amorphous silica system has been examined by both theoretical (Gambino et al. 2004) and spectroscopic (Kitadai et al. 2009) investigations. It was inferred that the adsorption was mainly driven by the electrostatic interaction between the positively charged side-chain amino group ($-\epsilon\text{NH}_3^+$) and the negatively charged silanol group ($-\text{SiO}^-$). The contribution from the α -amino group ($-\alpha\text{NH}_3^+$) was interpreted to be minor owing to its proximity to the α -carboxyl group ($-\alpha\text{COO}^-$). We used these reported characteristics, together with our experimental adsorption data at various pH, ionic strength, Lys concentration, and the solid/water ratio, to determine the reaction stoichiometry and the ETLM parameters for Lys on amorphous silica. The likely adsorption mode of L-lysine dimer (LysLys) was constrained by comparing the experimental results with ones for L-lysyl-glycine (LysGly) taking into account their differences in structural and electrostatic properties. The ETLM parameters thus obtained were used, in combination with the reported constant for the peptide bond formation in bulk water (Kitadai 2014), to calculate the Lys–LysLys equilibrium in the presence of amorphous silica under a wide variety of aqueous conditions. To the best of our knowledge, this study provides the first quantitative and comprehensive prediction for the mineral-promoted amino acid polymerization in water.

Experimental

Materials

Lys mono-hydrochloride (purity; $\geq 99.9\%$) was obtained from the Peptide Institute, and LysLys di-hydrochloride ($>99\%$) and LysGly mono-hydrochloride ($>99\%$) were from Bachem. Amorphous silica was purchased from Evonik (AEROSIL® 380), where the material is synthesized by the hydrolysis of SiCl_4 at $1000\text{ }^\circ\text{C}$ in a stream of H_2 and O_2 ($\text{SiCl}_4 + 2\text{H}_2 + \text{O}_2 \rightarrow \text{SiO}_2 + 4\text{HCl}$). The sample consists of aggregates of small spheres ($\sim 7\text{ nm}$ in diameter) having a reported surface area of $380 (\pm 30)\text{ m}^2\text{ g}^{-1}$ with a SiO_2 content of $>99.9\%$. Acid-base titration showed that the amorphous silica has a net negative charge at pH higher than 5.5 (Fig. 1; see below for the titration method). The surface charge shifted negatively with increasing pH and ionic strength (NaCl).

Acid–Base Titration

Potentiometric titration was conducted in a closed PFA vessel at room temperature ($\sim 25\text{ }^\circ\text{C}$) using a portable pH meter (Seven2Go Pro; Mettler Toledo) equipped with an electrode (InLab Expert Pro; Mettler Toledo). Sample suspension was prepared by mixing 0.1 g of amorphous silica with 100 mL of NaCl solution (concentration; $1, 10,$ or 100 mM), and was stirred at least 1 h before each experiment under N_2 gas flow ($>99.99995\%$; Kayama Oxygen, Japan, 100 mL min^{-1}). While keeping the N_2 gas flow, acid and base titrations were performed independently using reagent grade HCl and NaOH solutions (0.1 or 1 M ; Wako), respectively. A change of less than 0.01 pH units

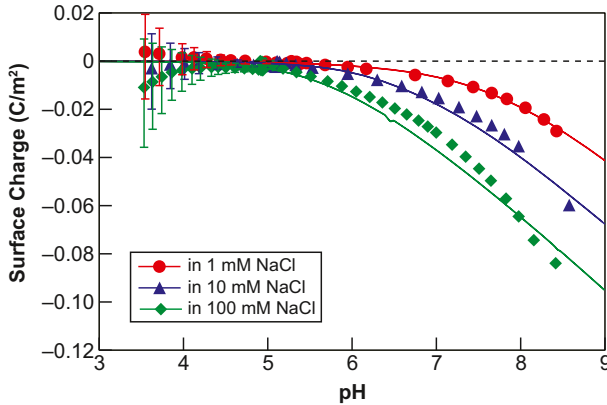


Fig. 1 Surface charge density of amorphous silica as a function of pH in 1, 10, and 100 mM NaCl solutions. Symbols denote the experimental acid-base titration data, whereas solid lines represent the ETLM calculation with the parameters presented in Table 2. Errors were estimated from the measurement error of pH (± 0.1)

over 3 min was used as the criterion for equilibrium. The surface charge, σ_0 (C m^{-1}), was calculated from the titration data using the following equation:

$$\sigma_0 = \frac{F}{A_s C_s} (C_A - C_B - [\text{H}^+] + [\text{OH}^-]) \quad (1)$$

Therein, F represents the Faraday constant ($96,485 \text{ C mol}^{-1}$), A_s stands for the surface area ($380 \text{ m}^2 \text{ g}^{-1}$), C_s denotes the solid/water ratio (1 g L^{-1}), C_A and C_B signify the net concentration of acid or base added to the solution, and $[\text{H}^+]$ and $[\text{OH}^-]$ represent proton and hydroxyl ion concentrations in bulk solution calculated from measured pH using the Davies equation (Drever 1997).

Adsorption Experiments

All adsorption experiments were conducted in a glove box filled with N_2 gas ($>99.99995\%$) at room temperature ($\sim 25^\circ \text{C}$). Sample suspensions were prepared by mixing 4 or 40 mg of amorphous silica with 4 mL of aqueous solutions with various pH, ionic strength (10 or 100 mM of NaCl) and organic adsorbate (0.1 or 1 mM of Lys, LysLys, or LysGly) in a 15 mL polypropylene centrifuge tube, and were rotated at 25 rpm for 24 h to adequately attain the adsorption equilibrium. The suspension was then measured for pH, centrifuged (8000 rpm, 10 min) and filtered with a PTFE membrane filter. Lys, LysLys, and LysGly concentrations in filtrates were quantified using a high performance liquid chromatograph (HPLC) equipped with a post-column derivatization system with *o*-phthalaldehyde (OPA) and a fluorescence detector operated at 345 nm for excitation and at 455 nm for emission (JASCO HPLC system). Five citrate buffer solutions with different citrate concentrations and pH were used as eluents in a stepwise condition. A cation-exchange column (Aapak Na II-S2; JASCO) was used at 50°C . The chromatograms for LysLys and LysGly showed no monomer signals (i.e., Lys and Gly), indicating that no peptide hydrolysis occurred during the adsorption experiment and the HPLC measurement. The overall reproducibility of the adsorption data was within $\pm 5\%$.

Thermodynamic Calculation

All equilibrium calculations were conducted using Visual MINTEQ (ver. 3.0; Royal Institute of Technology, Department of Land and Water Resources Engineering; <http://vminteq.lwr.kth.se/>) with the Davies equation for activity calculation (Drever 1997). The protonation constants of Lys, LysLys, and LysGly were taken from the NIST database (Martell et al. 2004; <https://www.nist.gov/srd/nist46>) (Table 1). The aqueous complexes between Lys (or Lys peptides) and electrolytes (Na^+ and Cl^-) were not taken into account because of the lack of relevant thermodynamic parameters for LysLys and LysGly in the literature. The mole fractions of Lys forming complexes with Na^+ and Cl^- , which are calculable with the reported constants (De Stefano and Sammartano 1993), are at most 10% in the conditions examined in this study. The small fractions had no appreciable influence on the regression calculation of the experimental adsorption data with the ETLM (data not shown). The same conclusion is expected to be made for LysLys and LysGly. In contrast, a strong influence on the solid/liquid distributions is expected in the presence of divalent metals (e.g., Ca^{2+} , Fe^{2+}) that have a wide variety of complexation constant with organic ligands.

Results and Discussion

Retrieval of the ETLM Parameters for Lys, LysLys, and LysGly Adsorption

The ETLM calculation for solute–surface interaction requires parameters for surface species and surface charge property in aqueous solution. Specifically, it requires the specific surface area (A_s), the surface site density (N_s), the inner and outer layer capacitances (C_1 and C_2), the surface protonation constants (K_1 and K_2), the electrolyte adsorption constants (K_{Na^+} and K_{Cl^-}), and, in our case, the adsorption constants for Lys, LysLys, and LysGly on amorphous silica. The value of A_s was assumed to be $380 \text{ m}^2 \text{ g}^{-1}$, and those of N_s , C_1 , C_2 , K_1 , K_2 and K_{Cl^-} were taken from Sverjenksy (2005) (Table 2). The value of K_{Na^+} was adjusted to optimize the theoretical reproduction of the surface charge data as a function of pH and NaCl concentration (Fig. 1). The adsorption constants for Lys, LysLys and LysGly were determined based on the experimental adsorption data taking into account the relevant spectroscopic and theoretical results reported previously (see below).

Figure 2 shows the adsorption of Lys (Fig. 2a), LysLys (Fig. 2b) and LysGly (Fig. 2c) on amorphous silica at various pH (3–9), NaCl concentration (10 or 100 mM), adsorbate

Table 1 Protonation constants of Lys, LysLys, and LysGly in bulk water. All values are taken from the NIST database (Martell et al. 2004)

Reaction	logK
$\text{Lys}^- + \text{H}^+ \rightarrow \text{Lys}^\pm$	10.66
$\text{Lys}^- + 2\text{H}^+ \rightarrow \text{Lys}^{2+}$	19.81
$\text{Lys}^- + 3\text{H}^+ \rightarrow \text{Lys}^{3+}$	21.96
$\text{LysLys}^- + \text{H}^+ \rightarrow \text{LysLys}^\pm$	10.90
$\text{LysLys}^- + 2\text{H}^+ \rightarrow \text{LysLys}^{2+}$	20.84
$\text{LysLys}^- + 3\text{H}^+ \rightarrow \text{LysLys}^{3+}$	28.26
$\text{LysLys}^- + 4\text{H}^+ \rightarrow \text{LysLys}^{4+}$	31.16
$\text{LysGly}^- + \text{H}^+ \rightarrow \text{LysGly}^\pm$	10.64
$\text{LysGly}^- + 2\text{H}^+ \rightarrow \text{LysGly}^{2+}$	18.30
$\text{LysGly}^- + 3\text{H}^+ \rightarrow \text{LysGly}^{3+}$	21.31

Table 2 Equilibrium parameters for the surface complexation of proton, electrolytes, and organic adsorbents (Lys, LysLys, and LysGly) on amorphous silica

Reaction	ψ^a	$\log K^{0b}$	$\log K^{0c}$	$\log K^{MFd}$
$>SiOH \rightarrow >SO^- + H^+$	$-\psi_0$	-8.24	-7.00 ^e	-8.24
$>SiOH + H^+ \rightarrow >SOH_2^+$	ψ_0	-2.64	-1.40 ^e	-2.64
$>SiOH + Na^+ \rightarrow >SiO^-Na^+ + H^+$	$-\psi_0 + \psi_\beta$	-6.25	-5.01	-6.25
$>SiOH + Cl^- + H^+ \rightarrow >SiOH_2^+Cl^-$	$\psi_0 - \psi_\beta$	-1.14	0.10 ^e	-1.14
$>SiOH + Lys^- \rightarrow >SiO^-Lys^\pm$	$-\psi_0$	5.90	7.14	5.90
$>SiOH + Lys^- + H^+ \rightarrow >SiO^-Lys^+$	$-\psi_0 + \psi_\beta$	13.90	15.14	13.90
$2 >SiOH + LysLys^- \rightarrow (>SiO^-)_2LysLys^+$	$-2\psi_0 + \psi_\beta$	13.34	17.82	10.80
$2 >SiOH + LysLys^- + H^+ \rightarrow (>SiO^-)_2LysLys^{2+}$	$-2\psi_0 + 2\psi_\beta$	19.94	24.42	17.40
$>SiOH + LysGly^- \rightarrow >SiO^-LysGly^\pm$	$-\psi_0$	5.30	6.54	5.30
$>SiOH + LysGly^- + H^+ \rightarrow >SiO^-LysGly^+$	$-\psi_0 + \psi_\beta$	12.40	13.64	12.40

^a Electrostatic factor

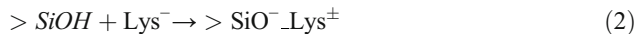
^b Molar concentration-based equilibrium constants corresponding to the site density ($N_s = 4.6$ sites nm^{-2}) (Sverjenksy 2005), the specific surface area ($A_s = 380$ $m^2 g^{-1}$), and the solid/water ratio ($C_s = 1$ $g L^{-1}$). Capacitance: $C_1 = 0.65$ $F m^{-2}$ and $C_2 = 0.65$ $F m^{-2}$ (Sverjenksy 2005). Note that the values for bidentate surface complexation depend on the solid/water ratio

^c Site occupancy-based equilibrium constants (Sverjenksy 2005). See (Wang and Giammar 2013) for the correlations among different thermodynamic expressions for the surface complexation reaction

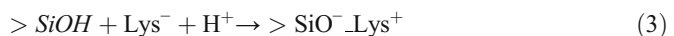
^d Mole fraction-based equilibrium constants as input in Visual Minteq

^e (Sverjenksy 2005)

concentration (0.1 or 1 mM), and the solid/water ratio (1 or 10 $g L^{-1}$). In all cases, no appreciable amount of adsorption was observed at pH below ~ 5.5 , while the values increased gradually at pH higher than the threshold. This result, and the tendency of lower adsorption at higher NaCl concentration (Fig. 2), indicate that a key binding mechanism is the electrostatic interaction between the negatively charged silica surface (Fig. 1) and the positively charged species of Lys and Lys peptides that are predominant at neutral and slightly alkaline pH (Fig. 3). For Lys on amorphous silica, In-situ ATR-IR spectroscopic analysis showed that Lys forms two outer-sphere surface complexes at pH from 7 to 10; one is the cationic state (Lys^+) and the other is the zwitterionic state (Lys^\pm), both of which have the positively charged ϵ -amino group ($-\epsilon NH_3^+$) (Kitadai et al. 2009). This observation may be represented by the following two equations (Fig. 4):



with the electrostatic factor (ψ) of $-\psi_0$, and



with $\psi = -\psi_0 + \psi_\beta$. We used these stoichiometries to regress the experimental adsorption data with the ETLM, and determined the equilibrium constant for each reaction (Table 2).

Unlike Lys, the surface bindings of LysLys and LysGly may occur via the $-\alpha NH_3^+$ group as well as the $-\epsilon NH_3^+$ group because the functional group is intramolecularly well separated from the $-\alpha COO^-$ group. The peptide nitrogen may also contribute to the adsorption. However, the adsorption of LysGly being rather low in comparison to Lys (Fig. 2a and c) denies the possibility, and the higher surface density of LysLys (Fig. 2b) suggests that the $-\epsilon NH_3^+$ group works as an important anchor for the peptide binding. Actually, it can be interpreted as the two

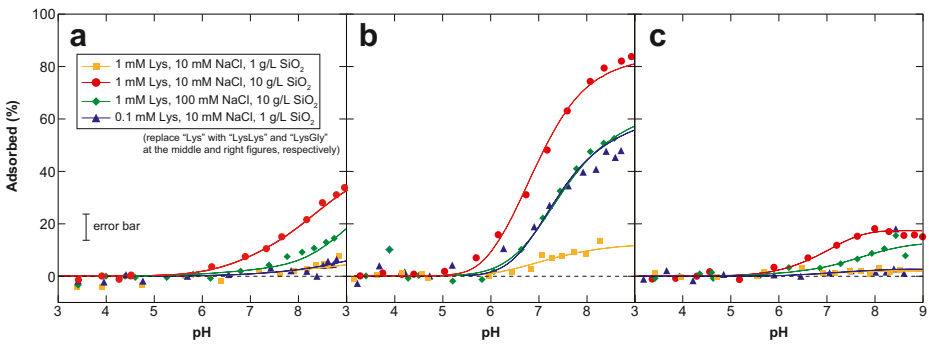
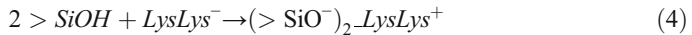


Fig. 2 Percentages of adsorbed Lys (a), LysLys (b), and LysGly (c) on amorphous silica at various pH (3–9), NaCl concentration (10 or 100 mM), the initial adsorbate concentration (0.1 or 1 mM), and the solid/water ratio (1 or 10 g L⁻¹). Symbols signify the experimental data, whereas solid curves represent the regression fits with the extended triple-layer model (ETLM)

-εNH₃⁺ groups in LysLys structure causing stronger interaction with the negatively charged silica surface than Lys does with one -εNH₃⁺ group. The carboxyl group of the adsorbed LysLys would be negatively charged because of the low protonation constant (logK = 2.90) (Martell et al. 2004), while the existence of both positive and neutral states of the α-amino group seems to be plausible, as is the case with the Lys adsorption. Consequently, we assumed the following two equations for the LysLys adsorption (Fig. 4):



with $\psi = -2\psi_0 + \psi_\beta$, and



with $\psi = -2\psi_0 + 2\psi_\beta$. The equilibrium constant for each reaction was determined by simultaneous regression of the adsorption data with the ETLM (Table 2). The occurrence of bidentate adsorption is supported from the molecular size information of LysLys and the silica surface; 2.8 Å for the

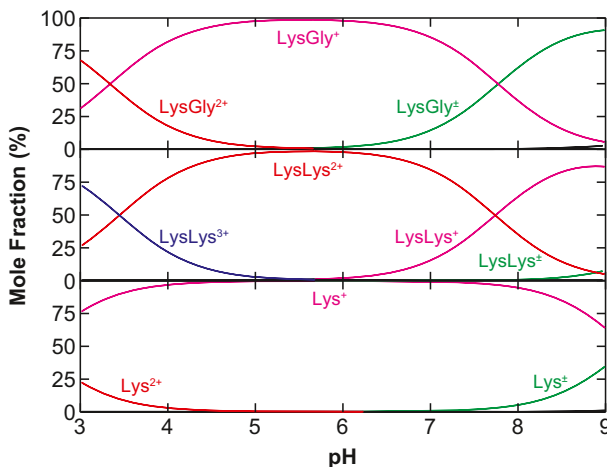


Fig. 3 Distribution of aqueous-phase species of Lys (bottom), LysLys (middle), and LysGly (top) as a function of pH calculated using the protonation constants listed in Table 1 assuming the ionic strength of 0.1

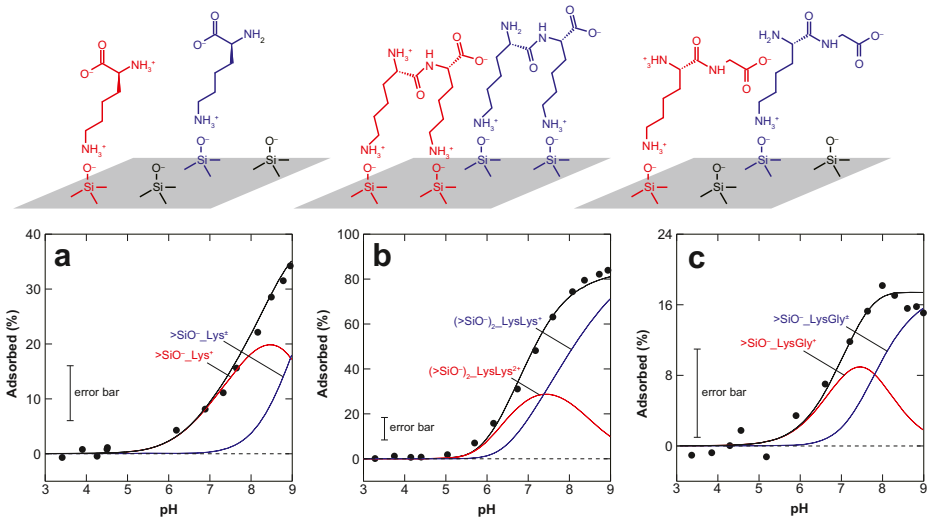


Fig. 4 Predicted surface species of (a) Lys, (b) LysLys, and (c) LysGly and their distributions as a function of pH in the presence of 10 mM of NaCl and 10 g L⁻¹ of amorphous silica. Filled circles correspond to the experimental data presented in Fig. 2 with the same symbols

distance of two side-chains connected through the peptide bond (Voet and Voet 2011), 4.7 Å for the mean distance between the surface silanol groups calculated from the density value (4.6 sites nm⁻¹), and 1.8–2.4 Å and 117–168° for the length and angle of the optimum >SiO⁻–εNH₃⁺ interaction predicted theoretically for Lys on silica (Gambino et al. 2004).

Finally, the LysGly on amorphous silica was described using the following two equations assuming similar adsorption behavior to that of Lys (Fig. 4):



with $\psi = -\psi_0$, and



with $\psi = -\psi_0 + \psi_\beta$. The corresponding equilibrium constants were determined by the ETLM regression calculation of the experimental adsorption data (Table 2).

As seen in Fig. 2, the ETLM reproduced all adsorption data adequately with the stoichiometries and the logK values listed in Table 2. Note that the occurrence of inner-sphere surface complexes (e.g., >SiOH + εNH₃⁺ → >SiNH- + H⁺ + H₂O, >SiOH + αCOO⁻ + H⁺ → >SiOC(O)- + H₂O) is unlikely for all systems because no covalent bond has been predicted theoretically for Lys on silica even in the absence of water molecules (i.e., in the gas phase) (Rimola et al. 2009). Cooperative adsorptions with Na⁺ and/or Cl⁻ (e.g., >SiOH + Lys⁻ + Cl⁻ + 2H⁺ → >SiO⁻Lys²⁺Cl⁻) are also improbable because higher NaCl concentration led to lower surface coverage of Lys, LysLys, and LysGly (Fig. 2). In fact, we conducted regression calculations with many possible adsorption stoichiometries, but no better fit with the experimental data was obtained than those presented in Fig. 2. The electrostatic interaction-induced adsorption has also been expected for Lys on highly dispersed silica (Vlasova and Golovkova 2004), for Lys on anatase (TiO₂) (Roddick-Lanzilotta et al. 1998), and for LysLys on anatase (Roddick-Lanzilotta and McQuillan 1999).

Thermodynamic Prediction of the Silica-Promoted Lys Dimerization

Could silica promote abiotic peptide bond formation on the primitive Earth? If so, what environmental condition was the best for this reaction? Here we calculate the monomer–dimer equilibria of Lys (0.1 mM) under various pH (3–9), NaCl concentration (1, 10, 100 mM), and the surface/water ratio (0, 10, 100, 1000 m² L⁻¹) using the ETLM parameters determined in this study (Table 2) in combination with the mean logK value for the peptide bond formation between $\alpha\text{-NH}_3^+$ and $\alpha\text{-COO}^-$ (logK = -2.98 at 25 °C) (Kitadai 2014). We did not conduct polymerization experiments of Lys because the reaction in water is expected to require a very long period, in the order of hundreds of years, to attain the equilibrium (Sakata et al. 2010). Results showed that the equilibrium shifts toward the dimer side with increasing surface/water ratio and with decreasing NaCl concentration at alkaline pH (Fig. 5a–c). At the optimum condition examined in this calculation (pH 9 in the presence of 1 mM NaCl and 1000 m² g⁻¹ SiO₂), LysLys exhibited equilibrium concentration around 50 times larger than that calculated without silica. 1 mM (or less concentration) of NaCl corresponds to freshwater in lakes, rivers, and underground, whereas 1000 m² L⁻¹ of SiO₂ corresponds to an infiltrating water in a silica pore with 4 μm diameter, which is the typical pore diameter seen in sandstone (Nelson 2009). The natural occurrence of alkaline pH has been observed in groundwater discharging from ultramafic rocks (Marques et al. 2008; Suda et al. 2014) and calcium silicates (Roadcap et al. 2005) Therefore, favorable conditions for the silica-promoted Lys dimerization is widely distributed in the terrestrial environments, and was probably widespread in the primitive ones as well (Maruyama et al. 2013). When Lys concentration in water is low, as was assumed in our calculation (0.1 mM), the thermodynamically attainable LysLys concentration is still dilute even in the presence of silica with a high surface/water ratio. However, it is noteworthy that LysLys was calculated to be mostly present in the adsorbed state at the conditions favorable for Lys dimerization (Fig. 5d–f). Because Lys and LysLys are expected to have preferred vertical orientations (Fig. 4) (Gambino et al. 2004), their interaction on the silica surface would be greatly advantageous for the intermolecular collision between $\alpha\text{-NH}_3^+$ and $\alpha\text{-COO}^-$ regarding

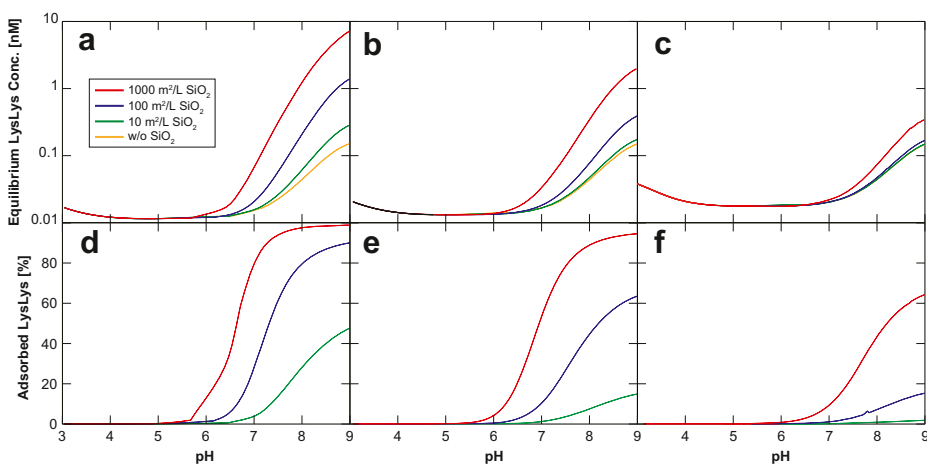


Fig. 5 Thermodynamic prediction of Lys (0.1 mM) dimerization to LysLys under various pH, NaCl concentration, and the silica surface/water ratio. (a–c) Total equilibrium LysLys concentrations (adsorbed + dissolved) in (a) 1 mM, (b) 10 mM, and (c) 100 mM NaCl. (d–f) Percentages of adsorbed LysLys in (d) 1 mM, (e) 10 mM, and (f) 100 mM NaCl

both geometry and density. It is also seen in Fig. 5d–f that the percentage of adsorbed LysLys has a great dependence on pH. Once Lys dimerizes on silica, a pH decrease from alkaline to acidic releases almost all adsorbed LysLys to the solution. pH changes can therefore prevent the reaction evolving into a dead end, and keep the surface to be available for newly adsorbed species. If the surface binding occurs along with dry heating (Rode 1999) and/or mixing with dehydration agents (Huber and Wächtersäuser 1998), their combination would further promote peptide bond formation on the surface. The peptides synthesized when simulating such environmental fluctuations (Rodriguez-Garcia et al. 2015) show characteristics in yield and variety that are consistent with the thermodynamic prediction made assuming the initial solution conditions (Sakata et al. 2010; Kitadai 2017). The methodology demonstrated in this study is therefore useful not only for the steady-state calculation of the mineral–water–amino acid interactions, but also for a theoretical survey of suitable situations for the amino acid polymerization in dynamic systems. Owing to the applicability, together with the versatility of the ETLM which was recently applied to describe the ribonucleotide adsorption on α - Al_2O_3 (Feuillie et al. 2015), future experiments with the reported methodology are expected to provide a significant constraint on the geological and geochemical settings that promoted the formation of biopolymers, and the subsequent chemical evolution of life.

Conclusion

This study presented a thermodynamic prediction of Lys dimerization on amorphous silica as a function of pH, NaCl concentration, and the surface/water ratio as the first example of quantitative evaluation of the mineral-promoted amino acid polymerization under various conditions. It was shown that the silica surface has a positive influence on Lys dimerization, and the influence varies greatly when changing all the parameters. To date, numerous experiments have been conducted to examine the polymerization behaviors of amino acids on minerals, but the current characterization of the dependency of reactivity on environmental parameters remains insufficient. The methodology demonstrated in this study is applicable to a wide variety of biomolecule–mineral combinations. Therefore, it can make a significant contribution toward elucidating suitable mineral species and environmental situations for the formation of biopolymers on the primitive Earth.

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