

Supporting Information for
Mechanism Associated with Kaolinite Intercalation with Urea:
Combination of Infrared Spectroscopy and Molecular Dynamics
Simulation Studies

Shuai Zhang,^{†,‡} Qinfu Liu,^{*,†} Feng Gao,[‡] Xiaoguang Li,[†] Cun Liu,[§] Hui Li,[‡] Stephen A. Boyd,[‡]
Cliff T. Johnston,^{||} and Brian J. Teppen^{*,‡}

[†]School of Geosciences and Surveying Engineering, China University of Mining
& Technology (Beijing), Beijing 100083, People's Republic of China

[‡]Department of Plant, Soil, and Microbial Sciences, Michigan State University, East Lansing,
Michigan 48824, United States

[§]Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science,
Chinese Academy of Sciences, Nanjing 210008, People's Republic of China

^{||}Crop, Soil and Environmental Sciences, Purdue University, West Lafayette, Indiana 47907,
United States

*To whom correspondence should be addressed.

Email: lqf@cumtb.edu.cn

Fax: +86 010 6233-1248

Email: teppen@msu.edu

Phone: 517-355-0271 ext. 1254

Force Field Energy Expression and Parameters

The CVFF-INTERFACE force field¹ was developed based on the CVFF force field² with the parameters developed for silicates, aluminates, metals, oxides, sulfates, and apatite to enable the simulations of inorganic-organic interfaces. The force field includes the potential energy terms and the corresponding parameters describing all atoms in the kaolinite framework. The OPLS-AA was used to define the urea model. Both force field employ the same harmonic energy expressions including quadratic bond stretching potential, quadratic angle bending potential, trigonometric torsion potential, Coulombic potential, and 12-6 Lennard-Jones potential with geometric combination rule. The energy (E) is the sum of contributions from each component as follows:

$$E = \sum_{Bond} K_r (r - r_0)^2 + \sum_{Angle} K_\theta (\theta - \theta_0)^2 + \sum_{Dihedral} K_\phi [1 + d \cos(n\phi)] + \sum_{i,j \text{ nonbonded}} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \sum_{i,j \text{ nonbonded}} \frac{q_i q_j}{r_{ij}}$$

where the first three terms represent the bond stretching, angle bending, and dihedral torsional terms which describe the intramolecular interactions of kaolinite and urea, and the last two terms are the Lennard-Jones potential (12-6 potential) and Coulombic potential energy terms which describe the intermolecular interactions between kaolinite surface and urea.

The force field parameters for kaolinite particles were taken from the CVFF-INTERFACE force field by Heinz et al.^{1,3} The parameters σ of van der Waals energy was adjusted due to the moderate difference in the type of 12-6 Lennard-Jones potential used in the LAMMPS package compared with that in the ref.³ Here, we only gave the nonbonded Lennard-Jones parameters and atomic charges for kaolinite in Table S1. Please see the other

parameters of bond stretching and angle bending in ref.³ The force field parameters for urea particles were directly taken from OPLS-AA force field⁴ except that the parameters for dihedral torsional terms were adopted from the work of Smith et al.⁵ These force field parameters were summarized in Table S2.

Table S1 Lennard-Jones parameters and atomic charges for kaolinite

Nonbond	Charge (<i>e</i>)	σ (Å)	ϵ (kcal/mol)
Si _{surface}	+1.1	3.5636	0.05
Al _{octahedral}	+1.45	3.7418	0.05
O _{surface}	-0.55	3.1182	0.025
O _{apical}	-0.758	3.1182	0.025
O _{hydroxyl}	-0.683	3.1182	0.025
H _{inner hydroxyl}	+0.2	0.9667	0.15
H _{inner surface hydroxyl}	+0.2	0.9667	0.15

Table S2 Force field parameters for urea

Nonbond	Charge (<i>e</i>)	σ (Å)	ϵ (kcal/mol)
C	+0.142	3.75	0.105
O	-0.39	2.96	0.21
N	-0.542	3.25	0.17
H	+0.333	0	0
Bond	r_o (Å)	K_r [kcal/(mol·Å ²)]	
C–O	1.229	570	
C–N	1.335	490	
N–H	1.01	434	
Angle	θ_o (degrees)	K_θ [kcal/(mol·rad ²)]	
O–C–N	122.9	80	
N–C–N	114.2	70	
C–N–H	119.8	35	
H–N–H	120	35	
Torsional dihedral	<i>d</i>	<i>n</i>	K_ϕ (kcal/mol)
O–C–N1–H1	-1	2	41.8
O–C–N2–H2	-1	2	41.8

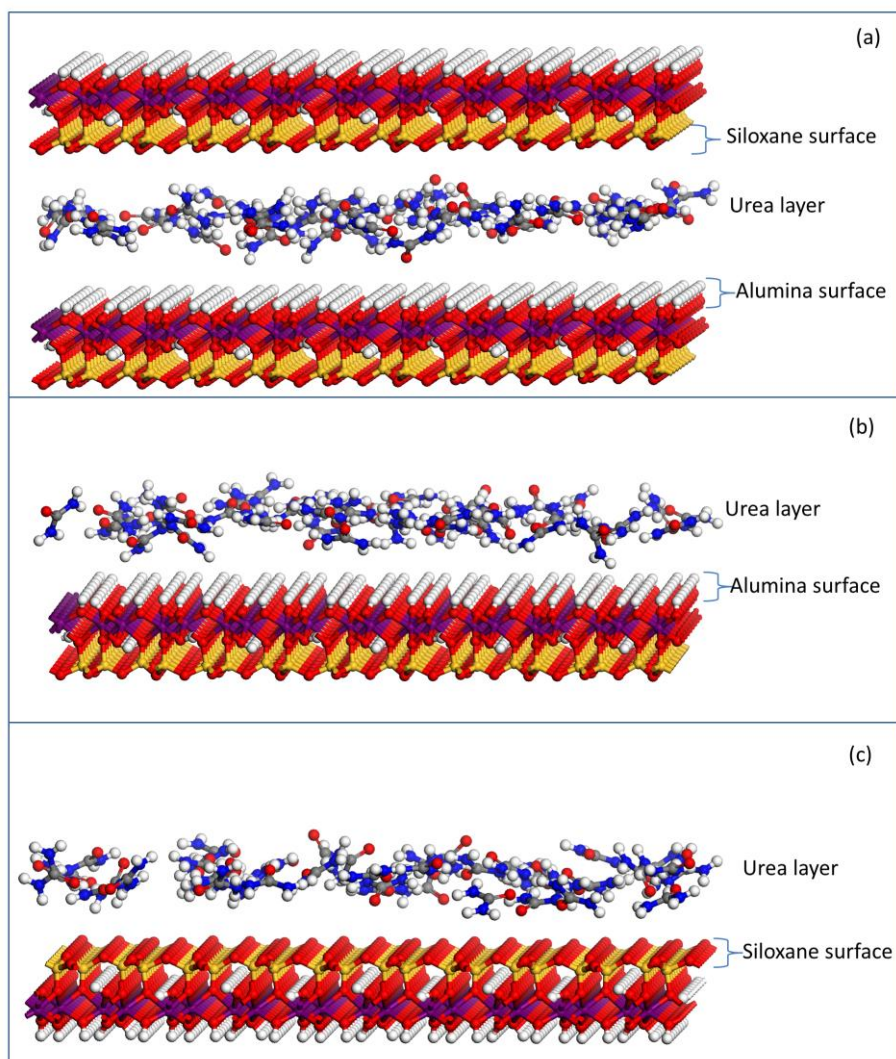


Figure S1. Initial configuration of the (a) $TO\bar{T}$, (b) TO , and (c) $\bar{T}O$ models. The ball color scheme for kaolinite layer is O, red; H, white; Si, orange; and Al, purple; for urea layer it is C, gray; N, blue; O, red; and H, white.

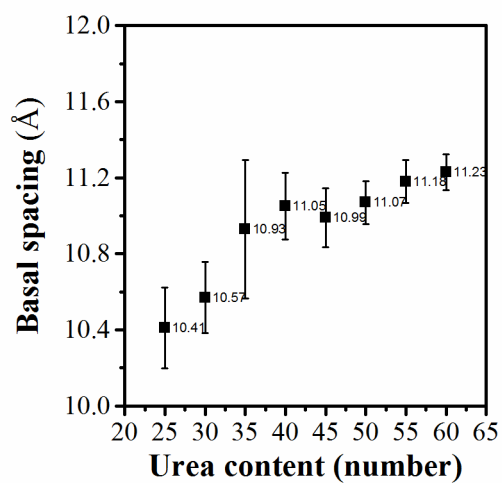


Figure S2. Basal spacing of kaolinite-urea intercalates with various urea contents calculated with MD

References

- (1) Heinz, H.; Lin, T.-J.; Kishore Mishra, R.; Emami, F. S., Thermodynamically Consistent Force Fields for the Assembly of Inorganic, Organic, and Biological Nanostructures: The Interface Force Field. *Langmuir* **2013**, *29*, 1754-1765.
- (2) Dauber-Osguthorpe, P.; Roberts, V. A.; Osguthorpe, D. J.; Wolff, J.; Genest, M.; Hagler, A. T., Structure and Energetics of Ligand Binding to Proteins: Escherichia Coli Dihydrofolate Reductase-Trimethoprim, a Drug-Receptor System. *Proteins Struct. Funct. Bioinf.* **1988**, *4*, 31-47.
- (3) Heinz, H.; Koerner, H.; Anderson, K. L.; Vaia, R. A.; Farmer, B. L., Force Field for Mica-Type Silicates and Dynamics of Octadecylammonium Chains Grafted to Montmorillonite. *Chem. Mater.* **2005**, *17*, 5658-5669.
- (4) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J., Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225-11236.
- (5) Smith, L. J.; Berendsen, H. J. C.; van Gunsteren, W. F., Computer Simulation of Urea-Water Mixtures: A Test of Force Field Parameters for Use in Biomolecular Simulation. *J. Phys. Chem. B* **2004**, *108*, 1065-1071.