Supporting Information for
Molecular Dynamics Simulation of Basal Spacing, Energetics, and Structure Evolution of a Kaolinite–Formamide Intercalation Complex and Their Interfacial Interaction

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The potential function of force field and force field parameters

The potential function of CVFF-Interface force field for kaolinite–formamide complex model is based on the CVFF as shown in the following equation.

$$E = \sum_{bonds} K_r\left(r - r_0\right)^2 + \sum_{angles} K_\theta\left(\theta - \theta_0\right)^2 + \sum_{dihedrals} K_\phi\left[1 + \cos\left(n\phi - d\right)\right] +$$
$$\sum_{i,j\ nonbonded} 4\varepsilon_{0,ij}\left[\left(\frac{\sigma_{0,ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{0,ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0\varepsilon_r}\sum_{i,j\ nonbonded}\frac{q_i q_j}{r_{ij}}$$

where the first three terms are the quadratic bond stretching potential, quadratic angle bending potential, and dihedral torsional potential, which compute the intramolecular interactions. The last two terms are the nonbonded 12-6 Lennard-Jones potential with geometric combination rule and Coulomb potential, which compute the intermolecular interactions.

For the clay mineral model, not all the CVFF energy terms are required. The quadratic bond stretching potential, quadratic angle bending potential, 12-6 Lennard-Jones potential with geometric combination rule, and Coulomb potential are considered[1,2]. The force field parameters for kaolinite model were taken from the CVFF-Interface force field, while the parameters of van der Waals energy were adjusted due to the moderate difference of the 12-6 Lennard-Jones potential used in the LAMMPS package with that employed in the CVFF-Interface force field. Here the parameters of 12-6 Lennard-Jones potential and atomic charges for kaolinite model were only listed in the Table S1, and the parameters of bond stretching potential and angle bending potential were given in the refs[1,2]. The force field parameters for formamide model were directly taken from the CVFF-Interface force field and given in the Table S2.

Table S1 Force field parameters of 12-6 Lennard-Jones potential and atomic charges for kaolinite model.

Nonbonded	Charge (*e*)	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	0.015
$H_{inner\ surface\ hydroxyl}$	0.2	0.9667	0.015

Table S2 Force field parameters for formamide model.

Nonbonded	Charge (*e*)	σ (Å)	ε (kcal/mol)
C	0.1668	3.617	0.148
O	–0.38	2.8598	0.228
H (HC=O)	0.2132	2.45	0.038
N	–0.56	3.5012	0.167
H (NH_2)	0.28	0	0
Bond	r_0 (Å)	K_r (kcal/(mol·Å^2))	
C–O	1.23	615.322	
C-H (HC=O)	1.105	340.618	
C–N	1.32	388	
N–H (NH_2)	1.026	457.46	
Angle	θ_0 (°)	K_θ (kcal/(mol·rad^2))	
H (HC=O)–C–O	120	55	
O–C–N	120	68	
H–C–N	120	45	
C–N–H	115	37.5	
H–N–H	125	33	
Dihedral	K_ϕ (kcal/mol)	*n*	*d* (°)
O–C–N–H (NH_2)	1.5	2	180
H (HC=O)–C–N–H (NH_2)	1.5	2	180

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) Heinz, H.; Koerner, H.; Anderson, K. L.; Vaia, R. A.; Farmer, B., Force Field for Mica-Type Silicates and Dynamics of Octadecylammonium Chains Grafted to Montmorillonite. *Chem. Mater.* **2005**, *17*, 5658-5669.