

An insight into flotation chemistry of pyrite with isomeric xanthates: A combined experimental and computational study

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1 Experimental

1.1 Adsorption kinetic studies

Kinetic studies were carried out by mixing an accurate mass of 50 ± 0.01 mg pyrite to a series of 100 ± 1 mL conical flasks filled with 25 ± 0.01 mL of 1 mmol/L diluted solutions. Solution pH was adjusted to 7 by adding 0.1 M of HCl or NaOH solutions. The conical flasks were then sealed and placed in a shaker and shaken at 150 rpm and 25°C. The adsorption time was set to 0, 3, 5, 10, 15, 20, 30, 60, 90, 120 min, respectively. After equilibrium, the solution was centrifuged for 3 min at 3500 rpm, and the supernatants were sampled for measurement. All the concentrations were measured at the wavelength corresponding to max absorbance, $\lambda_{\max} = 301$ nm, using a UV/vis spectrophotometer (PUXI, TU-1901). The experiments were repeated three times in the same conditions and the average values were reported.

1.2 Sorption isotherms studies

For sorption isotherms experiments, suspensions contained 500 ± 0.01 mg pyrite in 25 ± 0.01 mL xanthate solutions. The solution concentrations was set to 0, 5, 10, 12, 15, 18, 20, 30, 40 mmol/L, respectively. Solution pH was adjusted to 7 by adding 0.1 M of HCl or NaOH solutions. The conical flasks were then sealed and placed in a shaker and shaken for 90 min at 150 rpm and 25°C. After equilibrium, the solution was centrifuged for 3 min at 3500 rpm, and the supernatants were sampled for measurement. All the concentrations were measured at the wavelength corresponding to max absorbance, $\lambda_{\max} = 301$ nm, using a UV/vis spectrophotometer (PUXI, TU-1901). The experiments were repeated three times in the same conditions and the average values were reported.

2 Calculation details

2.1 Universal force field

Universal force field was chose to performed MD simulations for several reasons in this study. First of all, universal force field is a full coverage of the periodic table force field for molecular mechanics and MD simulations[1]. The potential energy is expressed as a sum of valence or bonded interactions and non-bonded interactions[2]:

$$E = E_R + E_\theta + E_\varphi + E_w + E_{vdw} + E_{el} \quad (1)$$

The bonded interactions consist of bond stretching (E_R), angular distortions (i.e., bond angle bending (E_θ), dihedral angle torsion (E_φ), and inversion (E_w)). The non-bonded interactions consist of van der Waals (E_{vdw}) and electrostatic (E_{el}) terms. Second, MD simulations have been intensively conducted to model the mineral-reagent interactions via universal force field by Pradip et al [3]. They have successfully demonstrated universal force field can be used to model the mineral-reagent systems with reasonable accuracy. A brief summary about their work was presented in the following sections. The universal force field optimized structural parameters for organic molecules compared well with those reported in literature. To establish the validity of the universal force field for modeling mineral surfaces, they also optimized their crystal structures and compared them with experimental measurements. They found that the universal force field predicted values of lattice

parameters were in reasonable agreement with those experimentally reported. In addition, universal force field can be also well applicable to the analog computation of minerals-ions-water systems through practice by Camara Moussa et al[4,5]. At last, in order to validate universal force field, a geometry optimization was performed via universal force field, and the results were summarized in Table S1.

Table S1 Comparison of universal optimized and experimental crystal structures of pyrite

Lattice parameters (Å)	
Universal predicted	Experimental
$a=b=c=5.416 \text{ Å}, \alpha=\beta=\gamma=90^\circ$	$a=b=c=5.418 \text{ Å}, \alpha=\beta=\gamma=90^\circ$

As shown in Table S1. The lattice parameters calculated were in good agreement with those obtained from the XRD data. In addition, the X-ray diffraction (XRD) spectrum of FeS₂ crystal was calculated via the Reflex module in Materials Studio, which matched well with the experimental spectra in Figure. 1. These results demonstrated that universal force field was a suitable force field for the pyrite crystal.

The XRD pattern of FeS₂ was calculated via the Reflex module in Materials studio 8.0. The specific parameters for simulating XRD patterns were as follows: 2-Theta: 5–80°, Radiation: X-ray, Profile function: Pseudo-voigt, peak shapes: asymmetry correction Rietveld.

2.2 Geometry Optimization

During simulations, all models were optimized by universal force field in Forcite module. First of all, the FeS₂ crystal, H₂O, Xanthates, activator, frother were optimized by universal force field. Second, the pyrite surface cell was created by cleaving the bulk unit cell of pyrite at the plane (100) using 3 layers of 4 × 4 FeS₂ units, which was also optimized by universal force field. Then, when the system was composed, it undergoes energy minimization by geometry optimization. At last, MD simulations were performed. For geometry optimization in Forcite module, the quality of the geometry optimization calculation is divided into Coarse, Medium, Fine and Ultra-fine. Actually, the quality level we chose is Fine in all MD simulations, which is reasonable for our present study. The default values of the convergence thresholds for each quality level are given in the Table S2.

Table S2 the convergence thresholds for each quality level

Value	Coarse	Medium	Fine	Ultra-fine
Energy(kcal·mol ⁻¹)	0.002	0.001	1×10 ⁻⁴	2×10 ⁻⁵
Force(kcal mol ⁻¹ ·Å ⁻¹)	2.5	0.5	0.005	0.001
Stress(Gpa)	2.5	0.5	0.005	0.001
Displacement(Å)	0.05	0.015	5×10 ⁻⁵	1×10 ⁻⁵

2.3 Build a solution model

Previously study[6] suggested that FeS₂(100) surface was the most stable surface. First of all, the pyrite surface cell was created by cleaving the bulk unit cell of pyrite at the plane (100) using 3 layers of 4 × 4 FeS₂ units with 0nm vacuum. Second, H₂O, activator and frother optimized were filled randomly to build a water box via AC module in Materials Studio. Then, pyrite surface and water box were connected by build layers tool. Finally, the reagent-mineral complexes were created by pasting the optimized xanthates to the optimized pyrite surface taking into account the interactions between Fe on pyrite surface and S of xanthates [7].

2.4 Simulation method

The MD simulations were carried out in constant number, constant volume and temperature (NVT) or constant number, constant volume and pressure (NPT) ensemble in this study because the ensemble could not be ascertained on the basis of existing literatures [8–10]. Each simulation was performed for NVT ensemble with the temperature fixed at 298 K or NPT ensemble with the pressure fixed at 1 atm. The minimization was performed using the Smart algorithm; the Ewald summation method and a cutoff of 1.25 nm were used to calculate the non-bonded interactions (Van der Waals and Coulomb interactions). Finally, 10 ns simulations were conducted to relax the system fully, and the trajectories of the last 1 ns were used for analysis. In order to determine the equilibrium, the RMSD was calculated via VMD 1.9.3[11]. Figure S1 demonstrates the RMSD of H₂O or isobutyl xanthate adsorbed on the surface of pyrite as a function of simulation time. As shown in Figure S1, there are little changes in RMSD for the components after about 8 ns in the system which indicates that the adsorption simulation has reached equilibrium. Thus, the total molecular dynamics time course of 10 ns was reasonable for obtaining optimized equilibrium configurations.

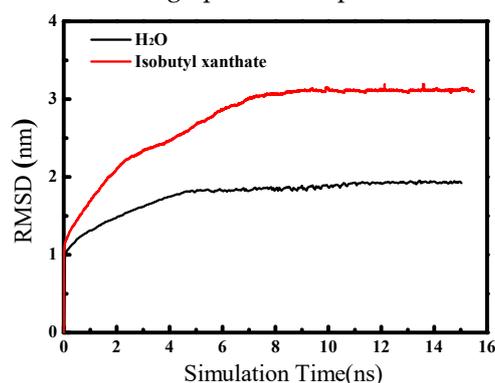


Figure S1 the RMSD of H₂O or isobutyl xanthate adsorbed on pyrite (100) surface in 10 numbers of complex xanthate solutions for NPT ensemble

2.5 DFT Calculation

The pyrite cell and molecular structures of the xanthates were geometrically optimized by density functional theory (DFT) with DNP basis set via the DMol3 module. DFT calculations within the generalized gradient approximation (GGA) using the Perdew, Burke and Ernzerhof (PBE) functional were carried out to calculation the xanthate molecules orbital (E_{HOMO} , E_{LUMO}), energy gap ($\Delta E_2 = E_{\text{LUMO}} - E_{\text{HOMO}}$) and dipole moment (μ). The values of the convergence thresholds in each quality level are given in the Table S3.

Table S3 the convergence thresholds for each quality level in DFT calculations

Value	Coarse	Medium	Fine
Energy(Hartree)	1×10^{-4}	2×10^{-5}	1×10^{-5}
Max.force(Hartree \AA^{-1})	0.02	0.004	0.002
Max.displacement(\AA)	0.05	0.005	0.005

Actually, the quality level we chose is Fine in all DFT calculations.

References

1. Rappe, A.K.; Casewit, C.J.; Colwell, K.S.; Iii, W.A.G.; Skiff, W.M. Uff, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
2. Leng, y.; Keffer, D.J.; Cumming, P.T. Structure and dynamics of a benzenedithiol monolayer on a Au(111) surface. *J. Phys. Chem. B.* **2003**, *107*, 11940–11950.
3. Pradip; Rai, B. Molecular modeling and rational design of flotation reagents. *Int. J. Miner. Process.* **2003**, *72*, 95–110.

4. Moussa, C.; Xu, J.; Wang, X.; Zhang, J.; Chen, Z.; Li, X. Molecular dynamics simulation of hydrated nantmorillonite with inorganic salts addition at high temperature and high pressure. *Appl. Clay. Sci.* **2017**, *146*, 206–215.
5. Zhang, X.; Yi, H.; Zhao, Y.; Min, F.; Song, S. Study on the differences of Na- and Ca-montmorillonites in crystalline swelling regime through molecular dynamics simulation. *Adv. Powder. Technol.* **2016**, *27*.
6. Hung, A.; Muscat, J.; Yarovsky, I.; Russo, S.P. Density-functional theory studies of pyrite FeS₂(100) and (110) surfaces. *Surf. Sci.* **2002**, *513*, 511–524.
7. Chen, J.; Lan, L.; Chen, Y. Computational simulation of adsorption and thermodynamic study of xanthate, dithiophosphate and dithiocarbamate on galena and pyrite surfaces. *Miner. Eng.* **2013**, *s 46–47*, 136–143.
8. Wang, L.; Hu, Y.; Sun, W.; Sun, Y. Molecular dynamics simulation study of the interaction of mixed cationic/anionic surfactants with muscovite. *Appl. Surf. Sci.* **2015**, *327*, 364–370.
9. Tian, S.; Erastova, V.; Lu, S.; Greenwell, H.C.; Underwood, T.; Xue, H.; Zeng, F.; Chen, G.; Wu, C.; Zhao, R. Understanding model crude oil component interactions on kaolinite silicate and aluminol surfaces: Towards improved understanding of shale oil recovery. *Energ. Fuel.* **2018**, *32*, 1155–1165.
10. Underwood, T.; Erastova, V.; Greenwell, H.C. Wetting effects and molecular adsorption at hydrated kaolinite clay mineral surfaces. *J. Phys. Chem. C.* **2016**, *120*.
11. Humphrey, W.; Dalke, A.; Schulten, K. Vmd: Visual molecular dynamics. *J. Mol. Graph.* **1996**, *14*, 33–38.



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