**Prediction of Hydrophobic Reagent for Flotation Process Using Molecular Modeling**

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**ABSTRACT:** The interaction or nonbonded energies of base organic ions and water molecules during the flotation process of minerals have important meanings for organizing hydrophobic and stable collectors. Furthermore, the interaction, cross-term, and valence energies of optimized structures are important for understanding the properties and structures of selective collectors. The simulation of pure scheelite mineral (PSM) surfaces with four different negative ions, using an adsorption locator module is demonstrated. The interaction energies for base organic ions and water molecules were resolved and detected by the adsorption locator module is demonstrated. The interaction energies for base organic ions and water molecules were resolved and detected by the adsorption locator module is demonstrated. The adsorption locator results for base organic ions and water molecules on PSM surfaces (112) and (101) using buffer width 0.5 Å and temperature range from 318.15 to 283.15 K confirmed the results obtain from Forcecite calculations. The results have demonstrated that the possibilities of using consistent valence force field implemented by Forcecite and adsorption locator modules in the selection of flotation reagents are cost saving. Furthermore, hydrophobicity of the main negative ions in soaps were solved by the simulation methods and results are in a good agreement with the experimental methods that proved that mustard soap is more selective on the mineral surfaces than sunflower soap when used as a collector. Increasing the molecular weight of negative ions increases the interaction energy between base collector ions and PSM surfaces (112) and (101) significantly.

**1. INTRODUCTION**

Most of the multiscale techniques and art molecular are described in detail before.1 Furthermore, simulation study was applied to search the interaction energies of a selection of organic surfactant molecules with the scheelite and calcium fluoride surfaces. The desired effect of the surfactant molecules was thus computed for the scheelite to be carboxylic acids (CAs) > alkyl hydroxamates (AHs) > hydroxy aldehydes (HAs) > alkyl amines (AAs) and for fluoiure AHS > CAs > HAs > AAs.2 The energies of interaction thus computed are significantly.

CVFF includes nonbonded parameters (the Born model) for extra force field types that are helpful for simulations of minerals, such as alumina phosphates, silicates, alumina silicates, and clays. These contributing parameters were gained by employing the Ewald summation for nonbonded interactions between the extra atom types.3 CVFF was suited to small organic molecules (such as amides, carboxylic acids, etc.) and gas phase structures. CVFF covers proteins, peptides, and a very large range of organic systems. CVFF has been applied in a widespread way for many years. CVFF is mainly proposed for analyses of structures and binding energies. Furthermore, CVFF can predict energies of conformational and vibrational frequencies fairly well.

The performance of CVFF is good for metals, minerals, and polymers.1,16–18 CVFF accomplishes more upper accuracy by cross-terms to report for such factors as angle distortions or bonds made near atoms. Dynamic properties of molecules and their experimental vibration frequencies were reported accurately by these terms. It can consist of the following: stretch–stretch, stretch–bend–stretch, bend–bend, torsion–stretch, torsion–bend–bend, bend–torsion–bend, and
stretch−torsion−stretch. CVFF earned full inclusion of Coulomb and Lennard-Jones interactions. Recently, accurate parameters for inorganic compounds have been inserted in the interface force field (IFF). The augmented IFF permits examining a very large indefinite number of new bioorganic interfaces with metals and minerals. IFF achieved power to describe experimental vibration of graphite accurately in the calculation of surface energy, hydration energy, and contact angle, more than CVFF, polymer consistent force field, chemistry at Harvard using molecular mechanics (CHARMM), and CHARMM new fit because it was supported by virtual electrons to account for cation−π, π−π stacking, H−π bonds, and solvent and organic interactions.

2. FORCITE AND ADSORPTION LOCATOR MODULES

The comparatively new module in Materials Studio is the adsorption locator, and it has been employed in several studies to find out binding sites and look into their energies, such as organic molecules on the surfaces of metal and nanoparticles. Adsorption locator is a simulation module that involves the greatest success of the Monte Carlo (MC) method in statistical mechanics in some generalized points such as the simulated annealing optimization method where an unreal temperature is applied and gradually decreased. An adsorbate loaded with a substrate or an adsorbate mixture of a fixed composition can be simulated by the adsorption locator, which helps us to discover low-energy adsorption sites on nonperiodic and periodic substrates and also to analyze the preferential adsorption of mixtures of adsorbate elements. Forcite is an advanced tool of the classical molecular mechanics (MM) method that gives quick energy computations and trustable optimized geometry of molecules and periodic system. A force field refers to any potential vibrations of a definite molecule in terms of some chosen set of internal coordinates. The MC method relies on statistical mechanics rather than molecular dynamics; instead of seeking to reproduce the dynamics of a system, it generates states according to appropriate Boltzmann probabilities. The MM method using classical physics relies on the force field with embedded parameters derived from the experiment and observation rather than theory. The energy results given by the adsorption locator were accurate for the comparison between base collector ions because the energy and minimization settings in the two modules were the same. This involves the CVFF, nonbonded summation methods, atomic charges, quality of the energy, geometry optimization calculations, and the convergence tolerances applied for the minimization. It was indicated that combination principles for nonbonded parameters between the inorganic and organic compounds accomplish well so that no extra parameters are required to simulate interfacial interactions.

2.1. Significance of Molecular Modeling

Mineral flotation is a promising modern area of molecular modeling, where the collector adsorbs onto water−mineral interfaces to control their hydrophilic or hydrophobic properties. The prediction of the structural features requires new and effective surfactants that could be accomplished by molecular modeling. It supplies detailed information and important understanding on subjects such as the potential of mineral surfaces, molecule adsorption, and floatatability of the mineral. In this article, a combination of MM and MC has been studied to generate logistic prediction for the behavior of different base solvents during flotation on the basis of interaction energy. Figure 1 summarizes the simulation steps used in this study.

The steps described in Figure 1 are accurate to generate logistic prediction for the interaction energy between negative ions of base collectors and pure scheelite mineral (PSM) surfaces during flotation. Because all energy minimization parameters and mineral surfaces were fixed constant except solvents in water, which were changed for each module, the total number of modules was eight because the study considered two PSM surfaces and four different base solvents.

![Figure 1. Demonstration of simulation steps used in Material Studio to predict the most hydrophobic base collector during flotation.](image-url)
reagents. The results obtained are helpful in qualitative analysis for the comparison between interaction energy of base solvents during flotation to predict the most selective base collector.

2.2. Liquid–Solid Nonbonded Energy. In this article, simulations have adopted a new methodology to demonstrate how MC and MM calculations available in Material Studio Version 8 could be fully applied for prediction of highly hydrophobic base reagent during flotation. Applying simulation to calculate interaction energy or nonbonded energy of the liquid–solid interfaces of various types of base collectors while fixing other parameters constant is not a difficult task. And simulation-generated accurate logic prediction helps us in the qualitative analysis of nonbonded energy. Furthermore, using the experimental method such as single pure mineral flotation where mustard and sunflower soaps were variables and all other parameters were kept constant to determine the best flotation performance by calculating recovery and analyzing concentrates using X-ray photoelectron spectroscopy (XPS) technique is very significant. Thus, XPS technique is an excellent experimental indicator for determining selectivity and hydrophobicity of the collector. Therefore, this study was intended to validate simulation results by XPS results.

3. TRADITIONAL AND NEW COLLECTORS

Nowadays, the prediction and design of highly hydrophobic reagents for flotation of scheelite represent a difficult problem in the industry. Excellent effect of mustard soap on the pure scheelite mineral surface (PSM) was observed through a trial-and-error method, after trying sunflower and bean nut soaps as collectors. The main compounds in mustard soap are erucate and 4-amino-2-hydroxybenzoate. It was made from natural materials and was inexpensive because mustard oil is cheap. It can be used as a collector, depressant, and frother for natural materials and was inexpensive because mustard oil is cheap.64 It was made from natural materials and was inexpensive because mustard oil is cheap.64 It can be used as a collector, depressant, and froth for the mineral processing.65 It is not impossible to synthesize many kinds of soaps from different oils, which have long-chain fatty acids (FAs), aromatic compounds, and functional groups and test each soap on the pure mineral surface as a collector to confirm which collector has better flotation efficiency. Molecular modeling can solve failures of a trial-and-error method to obtain a selective collector with low costs and save time by simulating industrial additives to obtain a selective reagent for the specific needs. Hydrophobic effect after the collector adsorption on the surface of mineral can be detected by experimental measurements, such as ζ-potential, flotation, XPS, Fourier transform infrared, and contact angle measurements. Screening and design of collectors developed for flotation of scheelite must take into consideration the different properties of mineral surfaces, such as a usually exposed cleavage and its stability, characteristics of calcium (Ca) sites, or energies of interaction between collectors and mineral surfaces.66 The most commonly exposed surfaces of scheelite particles are (112), (101), and (001) whereas the PSM surfaces at 112 and 101 exhibit different characteristics corresponding to past works, such as the investigation of sodium oleate gets the most effective adsorption on the surface 112, followed by surface 101. Additives of organic effect on crystal development processes proposed that collectors having two functional groups could either affect the morphology of surfaces or limit the development, whereas no particular effect was detected with collectors having a single functional group.55–59 In addition, studies in this domain intend to simulate erucate ions,66 oleate ions,59 and 4-amino-2-hydroxybenzoate (4-A-2-HB)66 on the PSM surfaces (112) and (101). Because they were used in the recent years for the Scheelite flotation, few researchers reported on the factors that determine the performance of combined reagents of aromatic compounds and carboxylate ions of the long chain as a collector. These findings were helpful for improving the scheelite separation.66

This article aimed to predict and understand the relationships of the behavior and properties of the two main compounds of mustard soap and different base organic ions and water molecules by employing CVFF. Furthermore, it also investigates the inside CVFF and MC to calculate interaction energies between atoms within each base’s organic ions and on the PSM surfaces (112) and (101) in the existence of water and base organic ions at logistic value, lower cost, and less time, since it is still not easy to reveal the interaction details by experimental measurements alone.65 The interaction, intra-molecular and adsorption energies of each base organic and water molecules have been averaged for the PSM surfaces (112) and (101), after using the MC calculations. Furthermore, a small water molecule after optimization, has been used for validation of experimental results, as demonstrated by Syouki.65 There is no research work done yet in this domain that investigates electronic structures of the two principal compounds of the mustard soap and main compound in the sunflower soap, on the PSM surfaces (112) and (101), using Forcite and adsorption locator modules.

4. RESULTS AND DISCUSSION

4.1. Geometry Optimization of Base Organic Ions and Water Molecules. Experimental data, calculated bond length (angstrom), and angles by CVFF for the water molecule after the geometry optimization process to validate the accuracy of force field used are demonstrated in Table 1.

| value of bond length (Å) | value of angle (deg) | force field | calculated bond length (Å) | calculated angle (deg) |
|-------------------------|---------------------|------------|---------------------------|------------------------|
| 0.96 ref 65             | 105                 | CVFF in Forcite module | 0.96                      | 104.501                |

Energies of optimized structures of each molecule analyzed using the function in Forcite module and study tables of all molecules are shown in the Table 2. Terms from 1 to 4 have been commonly referred to as the diagonal terms for the valence force field and represent the energy of deformation of bond lengths, bond angles, torsion angles, and inversion or out-of-plane interactions, respectively. Inversion energy is the energy needed to transform a molecule from one spatial form to another. It gives a good indication of the nature of the bonding between the atoms within a molecule.67 Terms 5 and 6 are commonly referred to as the diagonal terms for the nonbonded force field and represent the energy of interactions between the atoms within a molecule. Terms from 7 to 10 are off-diagonal (or cross) terms and represent couplings between deformations of internal coordinates. For example, term $S$ describes the coupling between stretching of adjacent bonds. These terms are required to accurately reproduce experimental vibration frequencies and therefore the dynamic properties of molecules. In some cases, research has also shown them to be important in accounting...
for structural deformations. However, cross-terms can become unstable when the structure is far from a minimum. 

Comparison between energies of optimized structures of base organic ions after geometry optimization was performed; this shows that the base organic ions had two or more functional groups and the interaction energy between their atoms is low as in the 4-amino-2-hydroxybenzoate and mixture of erucate-4-amino-2-hydroxybenzoate molecules. MM calculations have indicated that the mixtures of erucate with aromatic compound will be more hydrophobic on the PSM surfaces (112) and (101) than other molecules because it gave high valence and cross-term energies and lower potential and interaction energies due to the presence of carboxyl, hydroxyl, amino, aromatic, and hydrocarbon groups.

In Table 3, the elemental analyses of carbon, oxygen, and hydrogen are the most likely point of attachments between collector and PSM surfaces. The lower formal charge and higher molecular weight were −2 and 489.69, respectively, as found in the mixtures of erucate and 4-amino-2-hydroxybenzoate.

The optimized structures of oleate, erucate, 4-amino-2-hydroxybenzoate, erucate with 4-amino-hydroxybenzoate, and water molecules are demonstrated in Figure 2.

### Table 2. Comparisons between Contributions to Total Energy of Each Base Organic Ion and Water Molecule

| molecule                | a     | 1   | 2   | 3   | 4   | 5   | 6   | b   | c   | 7   | 8   | 9   | 10  | d |
|-------------------------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|
| 4-A-2-HB                | 22.84 | 10.28 | 1.22 | 0.00 | 0.00 | 33.09 | 22.54 | 11.50 | 10.55 | 0.92 | −0.05 | −0.03 | −0.06 | 0.79 |
| erucate-4-A-2-HB        | 47.51 | 10.98 | 4.91 | 6.20 | 0.04 | 44.94 | 20.60 | 22.13 | 24.33 | 0.96 | 0.25  | −0.01 | −0.16 | 1.04 |
| oleate                  | 36.34 | 1.08 | 2.80 | 2.95 | 0.05 | 10.13 | 18.86 | 6.88  | 28.99 | 0.06 | 0.40  | 0.00  | 0.01  | 0.48 |
| erucate                 | 42.04 | 1.24 | 2.95 | 3.25 | 0.01 | 11.98 | 22.24 | 7.45  | 34.22 | 0.07 | 0.36  | 0.00  | −0.05 | 0.38 |
| water                   | 0.00  | 0.00 | 0.00 | 0.00 | 0.00 | 0.00  | 0.00  | 0.00  | 0.00  | 0.00 | 0.00  | 0.00  | 0.00  | 0.00 |

Table 2, a, b, c, and d symbolize total potential, total valence, nonbonded, and total cross-term energies in kcal/mol.

### Table 3. Analysis Results for Optimized Structures Using chemBioDraw Ultra 12.0

| molecule                          | chemical formula | molecular weight | C    | H    | O    | N     |
|-----------------------------------|------------------|------------------|------|------|------|-------|
| 4-amino-2-hydroxybenzoate         | C 7H6NO3−        | 152.13           | 55.27| 3.98 | 31.55| 9.21  |
| oleate                            | C 18H33O2−       | 281.45           | 76.81| 11.82| 11.37|       |
| erucate                           | C 22H41O2−       | 337.56           | 78.28| 12.24| 9.48 |       |
| erucate-4-amino-2-hydroxybenzoate | C 29H47NO5−      | 489.69           | 71.13| 9.67 | 16.34| 2.86  |

For structural deformations. However, cross-terms can become unstable when the structure is far from a minimum. Comparison between energies of optimized structures of base organic ions after geometry optimization was performed; this shows that the base organic ions had two or more functional groups and the interaction energy between their atoms is low as in the 4-amino-2-hydroxybenzoate and mixture of erucate-4-amino-2-hydroxybenzoate molecules. MM calculations have indicated that the mixtures of erucate with aromatic compound will be more hydrophobic on the PSM surfaces (112) and (101) than other molecules because it gave high valence and cross-term energies and lower potential and interaction energies due to the presence of carboxyl, hydroxyl, amino, aromatic, and hydrocarbon groups.

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The optimized structures of oleate, erucate, 4-amino-2-hydroxybenzoate, erucate with 4-amino-hydroxybenzoate, and water molecules are demonstrated in Figure 2.

### 4.2. Properties of Scheelite.

Crystallographic parameters of PSM sample after X-ray diffraction (XRD) analysis are crystal system, tetragonal, space group: I41/a, space group number: 88, a (Å): 5.2429, b (Å): 5.2429, c (Å): 11.3730, α (deg): 90.0000, β (deg): 90.0000, γ (deg): 90.0000, calculated density (g/cm³): 6.12, measured density (g/cm³): 6.10, volume of cell (10⁶ pm³): 312.63, Z: 4.00, RIR: 2.49.

Orientation of the crystallographic parameter (hkl) was determined using XRD analysis results of PSM sample in Figure 2. The results of crystallographic parameters were obtained after XRD analysis for PSM sample with reference code 41-1431. This reference code is similar to that used for the simulation study that studies a similar structure of PSM sample using the adsorption locator module. The structure consists of blue, red, and yellow atoms, which represented the W, Ca, and O, respectively in the PSM. The structure of PSM is shown in Figures 3 and 4.

### 4.3. Monte-Carlo Simulation of PSM Surfaces (112) and (101) with Base Organic Ions and Water Molecules.

Outputs calculated by the Monte-Carlo simulation for adsorption of different organic and water molecules on PSM surface (112) and (101) are shown in Table S1 of the Supporting Information. The data within the Table S1 have included total energy in kcal/mol of the base organic ions and water constituents adsorbed on the PSM surfaces (112) and (101). The total amount of the energies of the organic and water molecules (the energy of rigid adsorption and the energy of deformation) have been characterized as the total energy. In addition, energy of adsorption in kcal/mol described energy released or needed when the relaxed base organic ions and water constituents adsorbed on the PSM surfaces (112) and (101). Energy of adsorption has been determined from the sum of the rigid adsorption energy and the deformation energy.
the base organic ions and water molecules could adsorb onto PSM surfaces (112) and (101) using the adsorption, interaction, and intramolecular energies to coat the crystalline of PSM surfaces (112) and (101), which greatly helped the flotation of the crystalline of PSM. In Figure 4a–d, cross-hair function supplied by Material studio software was used to determine the values of energy at the final step of the Monte Carlo method. Interaction energy was calculated in each system and averaged for PSM surfaces (112) and (101). Adsorption locator tool can be successfully employed to compute the interaction energies at the final step of the Monte Carlo method to compare between base collectors. Computed interaction energies are the nonbonded energies between the atoms of the surfactant and the calcium ions of PSM surfaces (112) and (101), in the presence of water molecules. The hydrophobic interaction referred to the interaction between atoms of hydrophobic tail of the base collector and calcium ions on the PSM surfaces (112) and (101) in the presence of water molecules, as found in Table S2 of the Supporting Information. A higher average value of interaction energy indicates the best hydrophobic interaction; see Figure 5a. The mixture from erucate and 4-amino-2-hydroxybenzoate was synthesized at the nanometer scale to compare its interaction energy on the PSM surfaces with that of other solvents at the nanometer scale and with experimental results. Therefore, mixtures containing erucate, hydroxyl, amino, and aromatic groups are more selective in coating the calcium ions of the PSM surfaces (112) and (101) than erucate > oleate > 4-amino-2-hydroxybenzoate because it contains carboxyl, hydroxyl, amino, aromatic, and hydrocarbon groups, which were in agreement with the findings from the literature reviews where excellent flotation performances had a good contribution in the field of mineral processing. The calculated energy type and interaction energy were tabulated for each system at the final step of the Monte Carlo method (2.5 × 10^5); also, minimum adsorption energy in each study table was reported (see the Supporting Information).

Hydrophobic interactions of base organic ions and water molecules on the PSM surfaces (112) and (101) are shown in Figure 5a–d.

The term hydrophobic was mentioned considering water molecules during the liquid–solid interfaces of each structure because the carboxylate ions had hydrophilic polar and hydrophobic nonpolar parts. Also, the aromatic compound had hydrophilic polar and hydrophobic nonpolar parts. During interactions, the effective part is the hydrophobic part. During the Monte Carlo rotation and translation steps, molecules containing erucate (C22) or mixtures of erucate and aromatic compounds have low mobility over the PSM surface (112) due to high interaction energy between negative ions of molecule and calcium ions through the PSM surfaces (112) and (101), whereas molecules containing oleate (C18) or aromatic compounds have high mobility over the PSM surface (112) and (101) due to low interaction energies; see Table S3 in the Supporting Information and Figure 5a in this article. During isosteric heating, water molecule energy was low but in the step sizes, its degree of rotation was high, if compared with another base organic ions. Increasing the molecular weight of negative ions in Table 3 increases the interaction energy between base collector ions and PSM surfaces (112) and (101) significantly, as shown in Figure 6a. In Figure 6a–c, the interaction, intramolecular, and adsorption energies for A or B or C or D base organic ions were increased or decreased.

Figure 3. XRD peaks of PSM and PDF number 41-1431.

Figure 4. Structure of PSM.
according to the increasing or decreasing of molecular weight of base collector, respectively. Thus, simulated mustard soap ions (A) have higher adsorption, intermolecular, and interaction energies, whereas 4-amino-2-hydroxybenzoate ions (D) have lower adsorption, intermolecular, and interaction energies. Therefore, two main ions of mustard

Figure 5. (a–d) Hydrophobic interaction of base organic ions and water molecules on the PSM surfaces (112) and (101).
soap are better than other base collector ions simulated, which include main ions of sunflower soap (oleate ions, C18). In the Figure 6a,c, K and M symbolize two engineering units (K = 10^3 and M = 10^6).

Because of the liquid–solid interactions, using base organic ions and water molecules on the PSM surfaces (112) and (101) leads to deformations of some of the bond lengths into the framework. These models are not presented here. However, their adsorption density fields are shown in Figure S1. For adsorption density profiles of base organic ions and water molecules on the PSM surfaces (112) and (101), see Figures 7 and 8. Results show that the adsorption energy of oleate or erucate ions on the PSM surface 112 is more than that on the PSM surface (101), whereas the adsorption energy of 4-A-2-HB or erucate-4-A-2-HB ions on PSM surface (101) is more than that on the PSM surface (112). This is due to differences in the interaction energies during interfaces between the PSM surfaces and the oleate or erucate or 4-A-2-HB or erucate-4-A-2-HB ions.

4.4. Gas Chromatography–Mass Spectrometry (GC–MS) Analysis Results. To analyze fatty acids in the sunflower soap, procedures from ref 30 have been employed, and the results demonstrated that retention time of 6.046 min was introduced from the contamination of the samples or from the GC–MS device. However, the quality of the results was not affected. The GC–MS results are illustrated in the Table 4 and Figure 9. These results showed that the main carboxylate ions in the sunflower soap are 9-octadecenoate ions (oleate ions).

4.5. XPS Analysis Results. To study the relationship between atomic concentrations on the surfaces of pure minerals after addition of soaps and simulated interaction energy during flotation of main ions in soaps, flotation concentrates were analyzed under similar test conditions for two samples at pH 11.3. Then, two flotation concentrates were filtered, dried, and analyzed using XPS technique. Then, XPS analysis results of two flotation concentrates using Casa XPS software version 2.3.17PR.1.1 was provided to calculate atomic concentration (%) on the surface of PSM. Figures 8, 9, and 10 showed that C 1s occupied 80.96, 62.79, and 32.22% on the surface of PSM after the addition of mustard and sunflower soaps and before addition of soaps, respectively, which revealed that negative ions of soaps adsorbed onto mineral surfaces. The addition of sunflower soap increased the amount of C 1s to 48.69%, whereas the addition of ions of mustard soap increased the amount of C 1s to 60.2% because the PSM has C 1s occupied 32.22%, which came from nature on mineral surfaces. High atomic concentration on the surface means the interaction energy between hydrophobic parts and calcium ions on the surface of PSM were high, as shown in Table 5.

Relation between simulated interaction energy and atomic concentration on the surfaces of PSM during flotation when using mustard and sunflower soaps as collectors gave the liner equation (y = 1.701x – 74.926) with R^2 = 1; see Figure 10. This indicated that recognition of hydrophobicity of the main negative ions in soaps by the simulation methods mentioned in this article are in good agreement with experimental results, which proved that mustard soap is more selective on the mineral surfaces than sunflower soap in use as a collector.
5. CONCLUSIONS

Molecule mechanics and Monte Carlo calculations were carried out to study the interaction of PSM surfaces (112) and (101) with four different ions. The predicted valence, nonbonded, and cross-term energies for each base organic ion were determined by carrying out MM tools in Forcite module using CVFF force field, followed by Monte Carlo calculations of the configuration space within the substrate–adsorbate system using CVFF force field. Interaction energy calculation shows that between the four base organic ions studied, the best hydrophobic molecules on the PSM surfaces (112) and (101) were mixtures, which contain erucate and aromatic compound compared with erucate > olate > 4-amino-2-hydroxybenzoate. Furthermore, simulation results showed that olate or erucate ions prefer to adsorb on the PSM surface (112) more than on the PSM surface (101), whereas 4-A-2-HB or erucate-4-A-2-HB ions prefer to adsorb on the PSM surface (101) more than on the PSM surface (112).

MM calculations indicated the hydrophobic phenomenon for the mixture of erucate and aromatic compound in terms of the ownership in the highest valence and cross-term energies and low interaction energies; however, results of final steps of MC have proven that the best hydrophobic interaction of liquid–solid interfaces occurs over the most stable suspension containing negative ions of low mobility due to high interaction energy. In methods described in refs 1 or 21 to obtain chemically and thermodynamically consistent force field parameters for new compounds using the IFF, it is required to calculate interaction energy by the experimental methods in ref 71. This task will be in the future, and it will not affect the qualitative results obtained in this article because the main purpose of this article was the prediction of the best hydrophobic base collector during flotation on the basis of nonbonded energy.

6. MATERIALS AND METHODS

6.1. Pure Scheelite and Its Surfaces (112) and (101).

Scheelite was purchased from Jutong Co. Jiangxi Province, China. Each sample was crushed and ground to fine particles employing a laboratory disk mill (Wuhan Rock Crush and Grand Equipment Manufacture CO., Ltd.). The purity of scheelite was 97.36%. The coordinates of atoms within the unit cell of the scheelite crystal have been investigated from the experimental structural reports based on X-ray studies.67−69

Cells of the periodic surface were established from the unit cells of the scheelite crystal at their cleavage plane.

6.2. Reagents.

Mustard soap72 and sunflower soap were synthesized by the same method described in ref 72. After different electronic structures were obtained, mixture from erucate and 4-amino-2-hydrobromate have been synthesized at the nanometer scale (see Table 3 in the results) to represent the two main compounds in the mustard soap, whereas the

Figure 7. Demonstrations of density profiles of base organic ions and water on the PSM surface (101).
main compound in the sunflower soap is oleate ions, as demonstrated in this article using GC−MS technique.

Table 4. GC−MS Results of Fatty Acids of Methyl Ester

| retention times (min) | library/ID | quality |
|-----------------------|------------|---------|
| 3.4039                | p-xylene   | 90      |
| 3.6998                | styrene    | 95      |
| 6.046                 | D-limonene | 98      |
| 14.9021               | heneicosane, 3-methyl- | 40 |
| 15.0078               | eicosane   | 92      |
| 21.7926               | pentadecanoic acid, 14-methyl-, methyl ester | 93 |
| 24.1598               | 9-octadecenoic acid, methyl ester, (E)- | 98 |

Figure 8. Demonstrations of density profiles of base organic ions and water on the PSM surface (112).

Figure 9. GC−MS output of esterified FAs of sodium carboxylates of sunflower soap.

Figure 10. Simulated interaction energy and atomic concentrations on the surfaces of PSM after different soap additions.

6.3. XRD Analysis. Characterization of the PSM was determined using the X-ray diffraction instrument model D8 advance, X’ Pert High Score Plus V3e software, Raw Data Origin ASCII.

6.4. Flotation Tests. The test conditions of scheelite flotation were using microflotation type (50 mL) purchased from Wuhan Rock Crush and Grand Equipment Manufacture Co., Ltd. PSM samples (2 g) were placed in deionized water (conditioning time, 1 min; rotating speed, 1850 rpm; 0.25 mL of a depressant Na2SiO3 (1.64 M); pH regulator Na2CO3 (0.2 g); and 2 mL of soap (0.02 g/mL)).

6.5. GC−MS Analysis. The FAs of the sunflower soap were converted to FA methyl ester using methods described in ref 72 to analyze the compositions by GC−MS using Agilent 6890.
with a manual sampling method and a mass selective detector. The FA methyl esters were named by comparing mass spectra with those of the National Institute of Standards and Technology (NIST) GC–MS database.

### 6.6. Simulation Details of Reagents and Water Molecules

MM and MC calculations force field,\(^\text{7,5,5}\) as implemented in Materials Studio, were used to optimize base organic ions and water molecules. CVFF is a generalized valence force field.\(^\text{61}\) In the CVFF force field, hydrogen bonds are a normal effect of the standard van der Waals (vdW) and electrostatic parameters; special functions of hydrogen bond do not develop the fit of CVFF to experimental data.\(^\text{66,77}\) Nonperiodic structures of these molecules were optimized as rigid molecules using Forcite module. Smart algorithm was used during geometric optimization.\(^\text{54}\) Partial charges within the atoms were computed by employing the method of QEq.\(^\text{78}\) whereas an atom-based method was used for nonbonded interactions. The cutoff distance for nonbonded interactions was fixed at 15.5 Å. A buffer width size 0.5 Å was used to create nonbonded neighbor lists for nonbonded interactions. The optimization was studied to be converged when a gradient of 1.0 × 10\(^{-4}\) kcal/mol was achieved. The maximum number of iterations was 500, which specifies the maximum number of geometry optimization cycles. The truncation method was cubic spline for nonbonded interactions, and the width of cubic spline was 1 Å. Intramolecular degrees of freedom of base organic ions and water molecules was not considered during geometry optimizations because it was estimated from sample data.\(^\text{39}\) Thereafter, motion groups were used to model rigid molecules to constrain the geometries of fragments or functional groups while allowing their location and orientation within a crystal cell to be optimized. A rigid molecule is composed of a group of atoms; the relative distances are fixed. Moreover, a rigid molecule inclines to cut down the degrees of freedom number required to identify the system configuration but it is effective in optimization of molecular crystal structures because they permit configurations of the known functional group to be preserved during optimization. In addition, it decreases the time of calculation for simulation.\(^\text{17}\) In this study, the Hessian matrix has been assumed for optimization methods and after the number of cycles was completed, the calculations have been stopped, even if the convergence criterion was not satisfied, and force field CVFF has gained the power to use automatic parameters when no definite parameters were given, as seen in the Supporting Information. The accuracy of CVFF force field after geometry optimization was validated by comparing the experimental data of a small water molecule\(^\text{65}\) with the calculated one, whereas the logistic accurate prediction of adsorption locator results were validated by XPS experimental results.

### 6.7. Simulation Details of Liquid–Solid Interactions

During liquid–solid interactions, the CVFF was adopted because it contains parameters for tungsten metal, calcium ions, base organic ions, water, and a variety of other functional groups. Therefore, it is suitable for the interface of scheelite with base organic ions and water molecules. The surface cells of PSM thus created with a cleavage plane (112) had fractional thickness and thickness of 2 and 6.21 Å, respectively. Thereafter, a (2 × 2) supercell was created to build 19.266 and 25 Å thicknesses of vacuum slab and crystal, respectively, whereas cleavage plane (101) had fractional thickness and thickness of 2 and 9.523 Å. Therefore, a (2 × 2) supercell has been created to build 16.12 and 25 Å thicknesses of vacuum slab and crystal, respectively, to expose more possible surface area for getting in the base organic ions and water molecules. The atoms of PSM surfaces were defined by making "an atom set" named target atoms, and the search region was then defined such that the distance between each of the target atoms was always equal to or less than the specified maximum adsorption distance.\(^\text{15}\) Lastly, the adsorption locator was selected to carry out calculation on PSM surface (112) and (101). The values 10.0 Å and 10 kcal/mol of maximum adsorption distance and fixed energy windows were adjusted, respectively. Simulation of annealing algorithm was used to carry out MC sampling at the fine quality level of simulation for base organic ions and water molecules on the PSM surface (112) and (101). The start and final temperatures were 318.15 and 283.15 K, respectively, whereas heating cycles and steps per cycle were 5 and 50 000, respectively. Optimized structures of base organic ions and water molecules were selected to set the value of loading 1:1S, respectively, on each PSM surface. A flow plane of low energy was determined by accomplishing a search of flexible MC of the configurational space for the base organic ions and water molecules with PSM surfaces (112) and (101), as the temperature gradually decreases. This process was duplicated to further distinguish a minimum local energy. The base organic ions and water molecules within the framework were rotated or translated in a random manner and settled around the PSM surfaces (112) and (101). From the steps of the above configurations, one could either accept or reject on the basis of the selection rules of Metropolis MC. PSM surfaces (112) and (102) were treated as a rigid body, with a manual sampling method and a mass selective detector. The FA methyl esters were named by comparing mass spectra with those of the National Institute of Standards and Technology (NIST) GC–MS database.
where the coordinates of each particle in a specified collection of particles were fixed relative to the coordinates of all other particles in the group. The motion of atoms of base organic ions and water molecules accrued in the surface or below it did not affect the dynamics of the base organic ions and water molecules. Fixing the atoms of PSM surfaces has accelerated the simulation process. The intramolecular degrees of freedom were considered for base organic ions and water molecules during liquid–solid interface as a motion group, and ratios between total rotation or translation were accepted and attempted. Theoretical data was generated by chemBioDraw Ultra 12.0 on the characterizations of the optimized molecules and utilized to compare with interaction energies of liquid–solid interfaces.

7. COMPUTATIONAL DETAILS

Molecular simulations are accomplished using Materials Studio (V. 8, Accelrys Ltd., San Diego). It combines two modules, Forcite (is the advanced tool of the classical MM that gives quick energy computations and trustable optimized geometry of molecules and periodic system20) and adsorption locator (simulation module involves the greatest success at (MC) method in statistical mechanics). Materials used in this article were from refs 80–84. The structure had an error because its chemical name was not the same as that of the website. Therefore, the structure was corrected according to the chemical name mentioned in the website and this article using the tools provided with the Material Studio software. The hydrogen atoms of the carboxyl group of all other structures of base organic ions have been deleted to simulate negative ions in water. And the formal charges for oxygen atoms were assigned. Thereafter, all hydrogen atoms of negative ions and acid have been adjusted and cleaned utilizing the sketch tool available in the software.

7.1. Monte Carlo (MC) Method. By experimentation, a molecular system is reported by a little number of factors, such as volume and temperature. The molecular configuration groups that meet this partial knowledge are called a configuration ensemble. An ensemble is reported by a distribution function, which acts as the probability of each configuration, in the ensemble. A configuration probability in the method of canonical ensemble is given by eq 1

\[ p_m = C \exp[-\beta E_m] \]  

where \( C \) is an arbitrary standardization constant, \( \beta \) is the temperature of reciprocity, and \( E_m \) is the total energy of configurations \( m \). The temperature of the reciprocal is given by eq 2

\[ \beta = \frac{1}{k_B T} \]  

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The total energy of the configuration \( m \) is calculated in agreement with the following eq 3

\[ E_m = E_m^{AA} + E_m^{AS} + U_m^A \]  

where \( E_m^{AA} \) is the intermolecular energy between the adsorbate molecules and \( E_m^{AS} \) is the energy of interaction between the adsorbate molecules and the substrate and \( U_m^A \) is the total intramolecular energy of the sorbate molecule. The intramolecular energy of the substrate is not involved because its structure is fixed during the simulation; thus, energy contributions are fixed and vanish because only energy differences play a role in these cases of calculations. The total intramolecular energy \( U_m^A \) is the sum of the intramolecular energy of all adsorbate components given by eq 4

\[ U_m^A = \sum_{i=1}^{N_m} \mu_{n, i} \]  

where \( m \) refers to the set of adsorbate loadings of all components in configuration \( m \); when MC simulation has started, the configuration requires various steps to adjust to the current temperature. A simulation is, therefore, separated into an equilibration and a production stage. The properties at the end of the simulation are based upon the production stage only. In the equilibration and production stages of the simulation, each step starts with the selection of a step type using the weights set at the start of the simulation. The type of step can be either a rotation or a translation. After a step, the type is selected and a random component is chosen and the step type applies to a random species of that component. For more details about MC and Metropolis MC methods used in this study, refer to refs 86–89.

7.2. Consistent-Valence Force Field (CVFF). The potential energy is a function of the atomic coordinates for a molecule of \( N \)-atoms. There are 3\( N \) atomic degrees of freedom but only 3\( N - 6 \) (3\( N - 5 \) for linear molecules) are yielded after degrees of freedom for molecular rotation and translation disappear. Therefore, there are 3\( N - 6 \) (or 3\( N - 5 \)) coordinates that describe the molecular structure and not the molecule’s orientation and coordinate in space. These 3\( N - 6 \) (or 3\( N - 5 \)) coordinates are named internal coordinates, and mostly the lengths of bond and angles of bond suited though not unique band. For instance, the internal structure of a water molecule could be defined by the two bond lengths (O–H) and the bond angle (H–O–H). These established a band of three internal coordinates \([3N - 6 = 3]\) for water. The behavior of bond stretching or compression was well reported by the function of Morse. The function of Morse is harmonic and correctly shows that more energy is needed to compact a bond by a certain quantity than to stretch it by the same quantity with reference to the equilibrium length. In the force field of MM, the initiating stage for describing bond compression and stretching is the harmonic approximation. The easiest approach is to employ a function of quadratic potential energy, \( E_i = K_i(l - l_i) \), where \( K_i \) is the force constant, \( l \) is the actual bond length, and \( l_i \) is the natural bond length, better described as the reference bond length. This reference value is in common but not the same as the bond length of equilibrium for that bond type in any true molecule. The bond length of equilibrium is an outcome of a balance between forces corresponding to \( K_i(l - l_i) \) and forces such as nonbonded force, which are external to the bond. The attractive or dispersion part of the van der Waals (vdW) potential is generally described by a term with a 6 power, whereas the repulsive part is described by a 12 power, as seen in the Lennard-Jones function 12–6,30 eq 5

\[ E_{\text{van der Waals}} = \sum \left( \frac{R_n}{R} \right)^{12} - 2 \left( \frac{R_n}{R} \right)^6 \]  

where the term \( R_n \) is the depth of the potential well and its unit is kcal/mol. \( R \) is the distance at which the potential reaches its minimum, and \( R_n \) is equilibrium distance, and its unit is angstrom.15
The computation of electrostatic interactions mostly is established by the function of Coulomb potential energy utilizing charges $q$ of the atom-centered point given by eq 6

$$E_{\text{electrostatic}} = \sum \frac{q_i q_j}{\varepsilon R}$$

where the terms $q_i$ and $q_j$ are partial charges for atoms $i$ and $j$, $\varepsilon$ is the relative dielectric constant. $C$ equal to 332.0647/(kcal/mol)/Å/e2 is a unit conversion factor.15

Cross-terms, which describe interactions between angles and bond, torsions and angles, and so on, are used in some of the more advanced force fields. Such terms gave accurate calculations. Cross-terms characterize structural features such as lengths of bond or angles of bond depending on the neighboring structural features. The function of angle-bending potential energy includes only the harmonic approximation of simple single terms such as torsion potential energy function.90

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00413.

Energy contributors using automatic parameters, outputs calculated by the Monte Carlo simulation, final steps of the Monte Carlo method, and rotation and translation steps (PDF)

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