The DFT Study of Salicylohydroxamic Acid and Methylenediphosphonic Acid as Collectors in Niobium Minerals Flotation

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ABSTRACT: In this paper, salicylohydroxamic acid (SA) and methylenediphosphonic acid (MDA) are investigated by the Density Functional Theory (DFT) and flotation test for studying niobium minerals flotation. The DFT computation results show that the two oxygen atoms in the dianion of SA charge more negative charges than other atoms do, and thus become their reactive center. Meanwhile, the SA dianions, MDA anions and MDA dianions show higher atomic charge value and HOMO (Highest Occupied Molecular Orbital) energy; hence they have stronger flotation ability for niobium minerals than that of other forms. The result of flotation test is consistent with DFT analysis. However, there is a conflict between the results of quantum chemistry analysis for the compare of flotation ability, and we cannot draw the explicit conclusion. Therefore, experiment is a more reliable tool for comparing the flotation capacity of compounds whose structures are very unlike one another.

Keywords: salicylohydroxamic acid; methylenediphosphonic acid; niobium mineral; density functional theory; flotation ability

1 INTRODUCTION

China Flotation is an effective way to obtain niobium resources. According to the flotation experiences, we know that salicylohydroxamic acid (SA) and methylenediphosphonic acid (MDA) are great collectors for niobium mineral flotation [1].

Hydroxamic acid is a kind of organic compounds which contain CONHOH groups and SA. In recent years, the coordination performance of hydroxamic acid and MDA with transition metal ions, alkaline-earth metal ions and some heavy metal ions has been studied [2]-[4]. These reports exhibit the capability of coordination of hydroxamic acid and MDA. As one kind of hydroxamic acid organic compound, SA has most characteristics that hydroxamic acid has.

In niobium mineral flotation, MDA as an effective collector has been studied in many reports. Ren et al. [5] studied the flotation of niobite, fersmite and ilmenorutile by using three collectors with different concentration and pH. The results indicated that MDA is an effective collector for niobium mineral. Meanwhile, IR and XPS spectra showed that the adsorption of MDA on three niobium minerals surface is chemical adsorption. Ni et al. [6] also studied the flotation reagents for niobium oxide mineral and indicated that MDA shows good collecting ability toward oxide niobium mineral. The study about SA as a collector in niobium mineral flotation is relatively rare, but there are still some articles about other hydroxamic acid compounds used for niobium mineral flotation for our references [7][8].

With the development of computer hardware technology and Quantum Chemistry Theory especially for Density Functional Theory (DFT), the structural information of collectors can be obtained conveniently by computation. Besides, researchers can develop new flotation reagents with less time and cost through computation. DFT has become a valuable tool for studying mineral flotation systems. Zhao et al [9] studied the quantum chemistry information about cyclohexyl hydroxamic acid and benzylohydroxamic acid by using DFT, connecting quantum chemistry analysis with collecting ability. As a result, cyclohexyl hydroxamic acid was proved to be a new effective collector in scheelite flotation. Liu et al [10] investigated the adsorption mechanism of thiophosphorous compounds to sulfide minerals by using DFT. The results gave an atomic level understanding of the adsorption activity and selectivity of collectors to metal...
and mineral surfaces, providing a potential approach on the molecule level to design new compounds for improving the flotation ability of valuable minerals.

In order to find out the flotation mechanism of SA and MDA to niobium minerals, we will study the structural information through DFT calculation. Meanwhile, we will try to compare the flotation capacity of SA and MDA by DFT since there are few relevant papers reporting the compare of flotation capacity of collectors whose structures are very unlike one another. Besides, mineral flotation tests are carried out to validate the theoretical analysis.

2 EXPERIMENTAL SECTION

2.1 Materials

High-purity columbite and hematite samples used in microflotation are obtained from Bayan Obo concentrator, Inner Mongolia (China). The X-ray diffraction analysis of the fersmite samples shows the main mineral is fersmite (Figure 1); the X-ray diffraction analysis of columbite shows the main mineral was columbite (Figure 2); The samples, for microflotation experiments, are prepared by dry hand-grinding pure crystals in a porcelain mortar and screening out the −74∼+38μm fractions.

The purity of salicylhydroxamic acid used in this experiment is 99%, which was produced by Sigma-Aldrich Co. And HCl (hydrochloric acid) and NaOH (sodium hydroxide) were used as pH regulators. All the reagents used in this study are of analytical grade. Deionized double distilled water was used for all tests. In order to explore the calcium ions influence on mineral flotation, we prepared a solution of calcium ions using calcium sulfate dihydrate.

2.2 Computational methods

In this paper, all the relevant analyses about quantum chemistry are performed by Gaussian 03. The original geometric configuration of SA and MDP are obtained from Cambridge Crystallographic Data Centre (CCDC). We take ions of flotation reagents into consideration owing to the ionization of flotation reagents in aqueous solutions. The geometry of molecules and ions are optimized by Gaussian with DFT methods at B3LYP/6-31+g(d), and the energy is calculated at the same basis set.

2.3 Mineral flotation test

The flotation tests are carried out in Hallimond tube. In each test, one sample (1.0g) is dispersed in beaker with distilled water for 1 min. The pH is adjusted by pH meter. Then add the solution and collectors to Hallimond tube to carry out flotation test for 5 min. Next, collect the samples which rise in the solution, filtering, drying and weighing. Finally the result is converted to floating rate.

3 RESULTS AND DISCUSSION

3.1 The stability analysis of two configurations of SA

There are keto and oxime configurations in the tautomers of hydroxamic acid. In the meantime, the molecules of SA are ionized to anions and dianions in aqueous solutions. These tautomers of SA and their ions are listed in Figure 3 and Figure 4. As a kind of hydroxamic acid organic compound, SA also exists in two configurations. The configuration energy calculated is given in Table 1, and the ∆E shown in Table 1 is the energy difference between keto and oxime tautomers in the same species form (∆E = ET (keto)-ET (oxime)).

Figure 1. X-ray diffractogram of the fersmite.

Figure 2. X-ray diffractogram of the columbite.

Figure 3. Two configurations of hydroxamic acids.
Table 1. The total energy of SA in different species forms.

| Forms     | Configurations | $E_T$/a.u. | $\Delta E$/a.u. |
|-----------|----------------|-------------|-----------------|
| Molecule  | Keto           | -551.356    | 0.001           |
| Anion     | Keto           | -550.784    | 0.031           |
|           | Oxime          | -550.815    | 0.031           |
| Dianion   | Keto           | -550.039    | 0.000           |
|           | Oxime          | -550.039    | 0.000           |

Table 1 indicates that the total energy of oxime configuration is lower than that of keto configuration for SA, which means oxime configuration is more stable in aqueous solutions. Hence, we mainly focus on studying oxime configuration for SA later.

3.2 The frontier molecular orbital analysis

The frontier molecular orbital (FMO) theory put forward by Fukui Kenichi [11] indicates that the highest occupied molecule orbital (HOMO) energy reflects electron-donating ability and the lowest unoccupied molecule orbital (LUMO) energy reflects electron-accepting ability.

The dipole moment reflects molecular polarity and interaction. The higher molecular polarity is, the bigger dipole moment is. Through calculation, the dipole moment and HOMO energy of SA and MDA are listed in Table 2 and Table 3.

The results indicate that the HOMO energy of dianion of SA and MDA is much bigger than their other species forms, thus their dianions has the strongest electron donation ability.

The dipole moment of SA follows the order: dianion>anion>molecule, hence the dianions of SA have stronger interaction to mineral surfaces. For the MDA, the dipole moment follows a different order: anion>dianion>trivalent anion>quadivalent anion>molecule, which means the force between the anion of MDA and the mineral is stronger.

Therefore, the dianion of SA and the anion or dianion of MDA has more chances to react with metal ions on minerals surface.

Meanwhile, the HOMO energy and dipole moment of the SA dianions are larger compared with the anion or dianion of MDA, which demonstrates that SA dianions show better collecting ability than MDA anions or dianions.

Table 2. The calculated HOMO energy and dipole moment ($\mu$) for SA.

| Forms     | $E_{HOMO}$/a.u. | $\mu$/D   |
|-----------|-----------------|-----------|
| Molecule  | -0.23003        | 1.6859    |
| Anion     | -0.03165        | 6.8083    |
| Dianion   | 0.17042         | 11.3539   |

Table 3. The calculated HOMO energy and dipole moment ($\mu$) for MDA.

| Forms        | $E_{HOMO}$/a.u. | $\mu$/D   |
|--------------|-----------------|-----------|
| Molecule     | -0.30752        | 1.2567    |
| Anion        | -0.12013        | 6.3393    |
| Dianion      | 0.04944         | 5.4773    |
| Trivalent anion | 0.02216      | 2.2591    |
| Quadivalent anion | 0.03523     | 1.6383    |

3.3 Natural charges

The schematic representation of SA and MDA and the calculated natural charges are listed in Figure 6, Table 4 and Table 5. The results show that for SA ions, the negative charges are mainly focused on O1 and O4 atoms in hydroxamic group. Hence O1 and O4 are the reactivity center, namely, O1 and O4 combined with metal ions on the surface of minerals form a five-member ring to collect the minerals. Overall, the two oxygen atoms of SA dianions have more negative charges, manifesting the stronger electron donation ability.

For MDA, different forms have different reactive places. Although the quadivalent anion of MDA has more negative charges, we should take the frontier molecular orbital analysis into consideration. Hence we still believe the anion or dianion of MDA has stronger electron donation ability.

Moreover, according to the dissociation constant of SA and MDA, the theoretical advantageous pH for the flotation of SA is a range which is greater than 7.4. For MDA, the favorable collecting pH range is about 2-5, which agrees with literature reported [5], [12].

Meanwhile, the anion and dianion of MDA exhibit more negative natural charges than the corresponding SA dianions, bringing about stronger collecting ability of the anion and dianion of MDA.
3.4 The binding model of collectors and niobium minerals

According to the analysis above, we give a possible bonding configuration of the SA with Fe$^{2+}$ and Ca$^{2+}$ in niobite and fersmite flotation, which is illustrated in Figure 6. In aqueous solutions, ionize the molecules of SA to anions, and then ionize the anions to the dianions which reacted with metal ions in mineral surfaces to float out niobium minerals. For the binding model of MDA, we found it hard to confirm the final results since the situation of active sites about MDA is complex.

Moreover, according to the dissociation constant of SA and MDA, the information of species forms of SA and MDA at different pH levels can be obtained. For SA, $\text{P}k_{a1}=7.4$. For MDA, $\text{p}K_{a1}<1$, $\text{p}K_{a2}=2.54$, $\text{p}K_{a3}=6.97$, $\text{p}K_{a4}=11.4$. Thus, we can speculate favorable collecting pH for SA is a range greater than 7.4. Besides, the advantageous pH range for the flotation of MDA is about 2-5.

3.5 The compare of collecting ability

We cannot compare the collecting ability in the same pH range since SA and MDA are different compounds, thus we compare the favorable forms for flotation only, i.e. MDA anions, MDA dianions and SA dianions.

However, the results of the frontier molecular orbital analysis contradict the results of natural charges analysis. We cannot judge which factor plays a more important role in the comparison, namely, we cannot compare the flotation capacity of those favorable forms. Hence, DFT calculation cannot be used for comparing the flotation ability of compounds whose structures are very unlike one another.

| Binding sites | Natural charges | Binding sites | Natural charges |
|---------------|-----------------|---------------|-----------------|
|               | Molecule | Anion | Dianion |
| O1            | -1.02816 | -1.04650 | -1.08445 |
| O2            | -1.02157 | -1.13597 | -1.19614 |
| O3            | -1.02835 | -1.06433 | -1.09046 |
| O4            | -1.05875 | -1.10684 | -1.10684 |
| O5            | -1.07527 | -1.11674 | -1.20164 |
| O6            | -1.07888 | -1.17043 | -1.21089 |

3.6 Flotation experiments of niobium minerals

The effect of pH on niobite and fersmite flotation with SA or MDA as collectors (50mg/L) is presented in Figure 7 and Figure 8. The flotation results show that the favorable pH for floating rate of niobium minerals (niobite and fersmite) by SA and MDA is about 8-10 and 2-5, respectively. These results agree with the analysis of DFT.
In the trial to compare the flotation ability of SA and MDA through experiments, we made another group of graphs by using the same data, which is illustrated in Figure 9 and Figure 10.

![Figure 9. The effect of pH on niobite floatability at 50 mg/L SA or MDA.](image)

![Figure 10. The effect of pH on fersmite at 50 mg/L SA or MDA.](image)

As we can see in the above figures, for niobite, the maximum floating rates of SA and MDA are 17.63% and 19.03%, respectively. For fersmite, the maximum floating rates of SA and MDA are 19.34% and 18.11%, respectively. Hence, there are no distinct differences for flotation capacity to niobium minerals between SA and MDA at their favorable conditions, which cannot be predicted by DFT analysis.

4 CONCLUSION

Based on the analysis above, it can be concluded that:

1. The dianion of SA and the anion or dianion of MDA have higher HOMO values and dipole moment than those of other species forms, which means they have stronger electron donation ability and flotation ability.

2. The charge population indicates that the negative charges are mainly dispersed in two oxygen atoms of SA, thus the two oxygen atoms are the reactive sites and would bind with metal ions on the surface of niobium minerals to form a five-member ring structure.

3. The results of the frontier molecular orbital analysis and natural charges analysis are inconsistent, which means the flotation ability of compounds whose structures are very unlike one another cannot be compared by suing DFT calculation.

4. In view of the imitation of DFT analysis, if we want to compare the flotation capacity of compounds whose structures are very unlike one another, we should do a lot of experiments and use the experimental data as a basis to analyze and study.

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