SYNERGIC EFFECT OF SODIUM OLEATE (NAOL) AND BENZOHYDROXAMIC ACID (BHA) ON FLOTATION OF WOLFRAMITE

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Abstract: In this work, two collectors sodium oleate (NaOL) and benzohydroxamic acid (BHA) were used to study the synergic effect in wolframite flotation. The flotation behaviour of these collectors was investigated at various NaOL:BHA ratios. Results show that the mixtures of NaOL with BHA of different ratios result in large improvements in the recovery of wolframite and the 9:1 NaOL:BHA ratio of collector mixture produced the highest wolframite recovery. The amount of NaOL and BHA adsorbed on wolframite was measured for these various reagent mixtures. Compared with pure NaOL, the addition of a certain proportion of BHA is beneficial for NaOL adsorption. Molecular dynamics simulations indicate the formation of HOL–HA (oleic acid–benzohydroxamic acid) complex can take place spontaneously in NaOL–BHA system. Additionally, HOL–HA complex interact with the huebnerite ($MnWO_4$) surface more easily than NaOL–HOL (the highest surface active composition in sodium oleate) and the addition of BHA enable the H of carboxyl group in HOL to generate hydrogen bonds with O atoms of huebnerite surface, resulting in a stronger affinity of mixed surfactants. These results reveal that in a binary NaOL–BHA system, the BHA can encourage greater adsorption of the NaOL.

Keywords: wolframit, mixed collector, molecular dynamics, synergic effect

Introduction

Since the discovery of tungsten in the last quarter of 18th century, tungsten-based products have been used in a wide range of applications from daily household necessities to highly specialized components of modern science and technology.

Nowadays, most tungsten ores contain less than 1% of WO_3 (Luo et al., 2003). Along with scheelite, the wolframite series are the most important tungsten ore minerals. An empirical formula of wolframite is $(Fe,Mn)WO_4$, an intermediate between two end–members: ferberite ($FeWO_4$) and huebnerite ($MnWO_4$).

Wolframite slimes are conventionally concentrated by a combination of gravity and magnetic separation techniques. However, the recovery of wolframite is lower than

45%. Therefore, apart from the gravity and magnetic separation operations, the concentration circuits usually include flotation.

Studies involving wolframite flotation have been carried out by many investigators. It is known that wolframite can be separated from the aqueous pulp as froth by using a fatty acid or its soap, or chelating agents as collecting agent. Hu et al. (1997) concluded that wolframite can be readily floated with chelating agents octyl hydroxamate at pH between 8 and 10. Wang et al. (1984) investigated the role of chelating collector with neutral oil for flotation of fine wolframite from coexisted gangues and obtained results indicated that compared with sodium oleate, chelating agents combined with neutral oil were more effective. A systematic fundamental study of the flotation behavior of wolframite with different components was carried out by Wang et al. (1986), who revealed that adsorption behavior and floatability of wolframite might be determined by the interaction between the agent and manganese ions of the mineral.

The benzohydroxamic acid (BHA) is a kind of organic compounds containing –CONHOH groups which mainly have two tautomers: keto-form and oxime-form. In wolframite flotation, benzohydroxamic acid (BHA) as effective collector have been studied in many reports. Gao et al. (2012) concluded that with the collector BHA, the preferable pH values for wolframite flotation was 8–10 and claimed that wolframite could chemically adsorb BHA on its surface. Xia et al. (2004) studied the quantum chemical property of BHA using semiempirical method PM3 (Parameterized Model Revision 3) and an *ab initio* method RHF (Restricted Hartree-Fork), results indicated that BHA existed mainly as keto-form and the five-member ring complex was formed through the two oxygen atoms of BHA with metal ions.

Composite collectors have been widely used for many years in flotation and a range of performance benefits have been reported for many different systems. Synergistic effects have been obtained greater than the sum of the parts and in some cases the mechanisms of this improved behaviour have been identified. Zhang and Somasundaran (2006) have studied the interactions between two surfactants in solution and at the air/liquid interface. The process benefits include increased pay metal recoveries and grades as well as increased rates of recovery whilst using lower dosages of reagents.

Wang et al. (2013) showed that in a BHA and sodium oleate system, the composite collector exhibited excellent collecting capacity and selectivity for complex and fine ore due to the complementation advantages of the composite collector (the high selectivity of BHA and strong collecting ability of NaOL). Although the use of composite collectors (the mixtures of BHA and sodium oleate collectors) for enhanced flotation and selectivity has been proposed to produce a synergistic effect and improve flotation performance, the action mechanism in flotation processes is still largely unidentified.

A study was carried out with the objective of elucidating the underlying action mechanism of the mixture of sodium oleate (NaOL) and benzohydroxamic acid (BHA) collectors in wolframite flotation.

Experimental

Mineral preparation

The wolframite sample was obtained from Jubankeng of the Guangdong province. The high-grade wolframite sample was hammered, separated by shaking table and dry magnetic separator, and then pulverized in a porcelain mill filled with agate balls. For experiments, +0.038 -0.074 mm fraction was used. Chemical analysis (Table 1) and X-ray diffraction (XRD) (Fig. 1) were used to study chemical and mineral compositions. The results show the purity of the wolframite to be roughly 99%.

Table 1. Elemental analysis results of wolframite

Component	WO_3	Mn	Fe	Pb
Content (%)	71.64	8.24	12.92	0.032

Reagents

The collectors of analytical grade used in this study were supplied by Chemistry and Chemical Engineering Institute of Central South University (China). Reagents were prepared on a daily basis using deionized water. Solutions of HCl and NaOH were used to adjust the pH of the system. Double distilled water was employed in all tests.
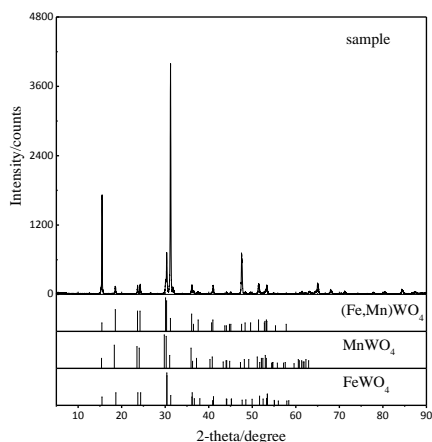
Flotation

Fig. 1. The XRD pattern of wolframite

Fig. 2. View of XFG laboratory flotation cell

As shown in Fig. 2, microflotation tests were carried out in a 40 cm^3 hitch groove flotation cell manufactured by XFG laboratory flotation (Jilin Prospecting Machinery Factory, China). The contents of the cell were stirred at 1920 rpm by a four-bladed impeller. Prepared mineral particles (2.0g) were dispersed in a plexiglass cell with distilled water for 1 min. The required pH of the slurry was adjusted by HCl or NaOH for 2 min. Then, the desired amount of reagents was introduced and the pulp was agitated for 5 min, followed by flotation for 5 min. The concentrate and the tailings were weighed respectively after filtration and drying to calculate the flotation recovery. The reported flotation recovery was averaged from at least three independent tests.

The measurement of adsorption quantity

The measurement of adsorption quantity of collectors on mineral surface was conducted by the Total Organic Carbon analyzer, manufactured by Shimadzu Japan. In adsorption experiments, wolframite particles (1g) were mixed with collectors of different concentration and shaken at 298K for 8h. The concentration of supernatant was measured after centrifugation at 5000 rpm for 10 min. Finally, the adsorption quantity of collectors on wolframite was calculated.

Molecular dynamics (MD) simulations

All calculations were performed in the framework of the molecular dynamics (MD) simulations using the Material Studio (MS) package. Firstly, CASTEP module included in MS software was adopted to build and optimize the crystal structure of huebnerite. By comparing different parameters to be optimized, the best optimization parameters were as follows: function GGA+WC, k-point set 4×4×4 and custom energy cutoff of 350 eV. The convergence tolerances for geometry optimization calculations using BFGS algorithm with Ultrasoft potentials scheme in reciprocal place were set to the maximum displacement of 0.0001 nm, maximum force of 0.3 eV·nm^{-1}, maximum energy change of $1.0×10^{-5}$ eV·atom^{-1} and maximum stress of 0.05 GPa. The SCF convergence tolerance was set to be $1.0×10^{-6}$ eV·atom^{-1}. The optimization results of the unit cell of huebnerite proved that the parameters used for the simulation were credible (see Table 2).

Table 2. Optimized results of the unit cell of huebnerite

Lattice constant	Analogue value	Experimental value (Weitzel, 1976)	error (%)
a	0.4807 nm	0.48238 nm	0.35
b	0.5788 nm	0.57504 nm	0.66
c	0.5024 nm	0.49901 nm	0.69
β	91.288°	91.18°	0.12

In the next stage, a 2D periodic surface cell was created from the 8×3×8 supercell of huebnerite at the complete cleavage plane (010) where the mineral crystal most

easily brakes (Anthony et al., 2003). Surface slabs were separated from repeated replicas by a 5 nm vacuum slab. Sodium oleate (NaOL), oleic acid (HOL) and Benzohydroxamic acid (BHA) molecules were separately optimized using UFF (Universal Forcefield) (Casewit et al., 1992; Rappe et al., 1993) as implemented in forcite module. Then, the optimized adsorbed molecule was just placed on the top mineral surface while the bottom-most layers were kept frozen. The initial geometry of the mineral surface-adsorbate molecule complex was created with the help of molecular graphics tools, taking into account the possible interactions of molecule functional groups with surface active sites. The molecule was relaxed completely on the surface using forcite geometry optimization. Since the configuration obtained with this method was only one of the possible adsorption modes, around 50 starting conformations were assessed so as to locate the minimum energy conformation of the molecule on the mineral surface. The most stable configuration of huebnerite surface-surfactant complex with the highest negative total energy was chosen for further molecular dynamics (MD) simulations.

Finally, forcite module was employed to calculate adsorption energies. NaOL, BHA and mixed NaOL–BHA were an adsorbate, huebnerite was an adsorbent. At first, the geometry optimization of the system of reagent-huebnerite was conducted using Smart Minimizer in UFF. MD simulations were run using NVT at 298 K with the time step of 1 fs. Total run length was 300 ps.

The structure of the complex obtained through the static energy minimization method represents only a local minimum energy structure which was used as the initial configuration to find out a global minimum energy structure through molecular dynamics (MD) simulations. The forcite module was used to perform a dynamics simulation using a NVT ensemble at 298 K with time step of 1 fs and 300,000 steps where the UFF was also employed. During the simulations, the temperature was controlled with an Andersen method and an atom-based cutoff method was employed for calculating both van der Waals and electrostatic interactions. Atom-based cutoffs were used with a 1nm cutoff distance. In order to smoothly turn off the interactions, the switching function was applied with a spline width of 0.1 nm and a buffer width of 0.05 nm.

The interaction energy ($E_{binding}$) of adsorbate molecules with mineral surfaces can be expressed by Eq. 1 (Rai et al., 2011; Wang et al., 2015):

$$E_{binding} = E_{complex} - E_{surface} - E_{adsorbate} \tag{1}$$

where $E_{complex}$ is the total energy of the optimized mineral surface-adsorbate molecule complex, while $E_{surface}$ and $E_{adsorbate}$ are the total energies of free mineral surface and adsorbate molecules respectively which are computed separately. Different modality has a different associate energy. Therefore, a negative value of associated energy indicates the association occurs spontaneously. The magnitude of this quantity is thus an excellent measure of the relative intensity of interaction.

Results and discussion

Flotation

Fig. 3 shows the flotation responses of wolframite as a function of pH with NaOL and BHA. As seen in Fig. 3, the curve of the two collectors demonstrated similar trend, having the maximum recovery at about pH = 9.0, and there is a dramatic decreasing of recovery under the acidic and strong alkaline condition. However, the recovery of wolframite by NaOL is significantly higher than BHA in the experiment with pH between 2 and 12 where the peak is at about pH=9, NaOL and BHA floated 65.8% and 15.1% of wolframite respectively. This shows that the collection capacity of NaOL is significantly stronger than BHA. In all further flotation tests pH was 9.
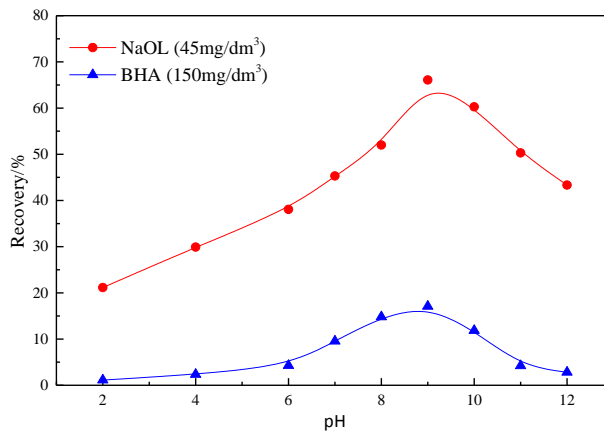

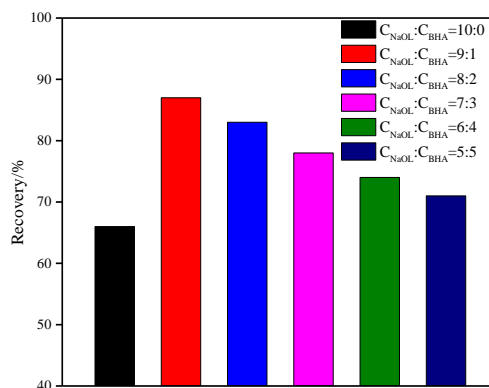Fig. 3. The recovery of wolframite as a function of pH at 298 K

Fig. 4. Recovery of wolframite at various ratios of NaOL and BHA
($C_{NaOL} + C_{BHA}$=45 mg/dm^3, pH=9)

Figure 4 shows the flotation behavior of wolframite using NaOL and BHA mixtures of different ratios as collector. The experiments were performed with 10:0, 9:1 and 8:2 ratios of NaOL:BHA in mixtures. The first value indicates the ratio of NaOL in the mixture and the second one BHA. Total collector concentration of the mixtures was taken as 45 mg/dm^3. It can be seen from Fig. 4 that all mixtures of different ratios can improve the recovery of wolframite to varying degrees. The most notable result was that a 9:1 NaOL:BHA mixture increased the recovery of wolframite by 21% beyond that of a pure NaOL.

Adsorption of NaOL and BHA on wolframite surfaces

The adsorption mechanism of mixture of the collectors was investigated at different ratios of NaOL and BHA by using TOC analyzer at pH 9.0. The adsorption amounts of NaOL and BHA on the surface of wolframite samples at various ratios of NaOL and BHA ratios were thus calculated. Calculated adsorption shown in Fig. 5 indicates that the amount of BHA adsorbed on wolframite increases with the increase of concentration of BHA in mixtures. However, it is interesting to note that at 9:1 and 8:2 ratios the amounts of adsorbed NaOL are considerably high, even higher than the amount adsorbed when NaOL is used as the only collector. Moreover, small amount of BHA also adsorbs in these condition, which in turn increases the total amount of collector adsorbed on wolframite. This can indicate that the addition of BHA improves the adsorption behavior of NaOL. The results of NaOL adsorption on wolframite correlate well with that of wolframite floatability.
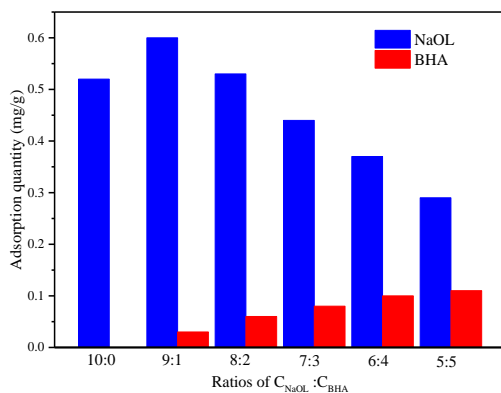

Fig. 5. Adsorption of collectors from the mixtures of NaOL and BHA
on wolframite surface at pH 9.0 ($C_{NaOL} + C_{BHA}$=45 mg/dm^3)

The flotation and the measurement of adsorption quantity approaches were employed to study the synergistic effect for NaOL/BHA collectors on wolframite flotation in the previous section. It can be concluded that the selected NaOL/BHA mixtures could increase the mineral recovery and adsorption amounts over and above

that of the single NaOL collector. In the following section, it is intended to compare the interaction activity of the NaOL, BHA and NaOL–BHA collectors with wolframite through MD simulation.

Molecular dynamics (MD) simulations

Property of huebnerite and collectors

The wolframite series consists of a complete solid solution $Fe_xMn_{1-x}WO_4$ present in nature with $0 \leq x \leq 1$, which is the principal source of tungsten. The end-members, the ferberite ($x = 1$; opaque black) and the huebnerite ($x = 0$; yellow red), show similar crystallographic structures (Blackburn and Dennen, 1988; Sleight, 1972). The relationship between flotation and Fe/Mn ratio of wolframite has been investigated. Some researchers consider that flotation of wolframite is determined by manganium (Mn) ions of wolframite surface (McLaren, 1943; Wang et al., 1986). Thus, the adsorption mode of the crystal structure that was selected in this study was huebnerite. The huebnerite crystallographic structure is monoclinic (pseudo-orthorhombic) with a space group *P2/c.* The oxygen ions form a distorted hexagonal close-packed structure such that one-half of the octahedra holes is filled with Mn ions and the other half with W ions. Layers of Mn ions alternate with layers of W ions (Klein and Geller, 1974). One important macroscopic feature is the perfect cleavage observed in the (010) plane. In this study the perfect cleavage crystal surface (010) of huebnerite was selected.

Both NaOL and BHA can undergo series of hydrolysis reactions in aqueous solution yielding complex species under appropriate solution pH conditions (Wang and Hu, 1988). In this study, the species considered are as follows: oleate ion (OL⁻), oleic acid (HOL) and oleic acid-soap complex (OL⁻–HOL) in NaOL solution; benzohydroxamic acid (HA) and benzohydroxamic ion (A⁻) in BHA solution. In the NaOL–BHA system, it is supposed to generate oleic acid-benzohydroxamic acid (HOL–HA) complexes. The adsorption mode of the oleate ion (OL⁻), oleic acid (HOL), oleic acid-soap complex (OL⁻–HOL), benzohydroxamic acid (HA), benzohydroxamic ion (A⁻) and oleic acid-benzohydroxamic acid complex (HOL–HA) on the huebnerite surface (010) were determined in this study.

Molecular dynamics (MD) simulation results and discussion

Molecular dynamics (MD) simulations are a valuable tool to study surfactant adsorption on solid surfaces at the microscopic level (Xu et al., 2014). Moreover, MD simulation can elucidate the dynamic characteristics of the adsorption process (Nikjoo et al., 2001). The interaction energy can be used as an indicator to measure the relative intensity/efficiency of interaction of different collectors with the mineral surface (Rai et al., 2011). The indicator makes sense because of its valid utility in designing or screening out the appropriate surfactants. Results of calculated interaction energy between the collectors and huebnerite surface (010) are shown in Fig. 6. As expected, NaOL should be more favorable for adsorption on wolframite than BHA. As shown in Fig. 6, the computed interaction energies for NaOL (HOL, OL⁻and OL⁻–HOL) and

BHA (HA and A⁻) on the huebnerite surface (010) indeed substantiate this conclusion. Additionally, the value of interaction energy between oleic acid-soap complex (OL⁻–HOL) and the surface is largest as compared to oleate ion (OL⁻) and oleic acid (HOL). This result compares well with the experimental findings by Ananthpadmanabhan et al. (1979) where the hydrophobicity of ionic oleic acid is strengthened by associating with molecular oleic acid and the bonding ability of COO⁻ on minerals surface is improved as well. The most important point to note is that in spite of the intensified adsorption ability of forming acid-soap (OL⁻–HOL) species for single NaOL collector, the value interaction energy between HOL–HA complex and the surface is larger compared with oleic acid-soap. Furthermore, the calculated associated energy of HOL–HA complex is –15.32 KJ/mol. Since a negative value of associated energy indicates that the association occurs spontaneously, the formation of HOL–HA complex can occur spontaneously in NaOL–BHA system. Above all, it can be concluded with certainty that the strength of interactions of HOL–HA–huebnerite surface excels the strength of interactions OL⁻–HOL–huebnerite surface and the BHA can encourage greater adsorption of the NaOL on wolframite surface.
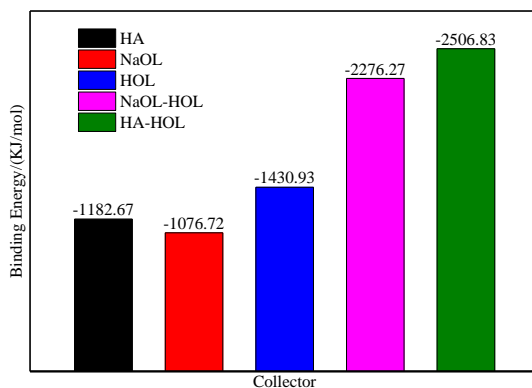

Fig. 6. Interaction energies computed theoretically
to show collector molecule on the huebnerite surfaces

Huebnerite structure may be described as made up of hexagonal close packed oxygen atoms with some octahedral sites filled in an orderly way with tungsten(VI) and manganese(II). A unit cell has half of the oxygen atoms coordinated to two tungsten atoms and half coordinated to two divalent cations. This atomic arrangement is adopted by divalent cations (Mn^{2+}) with ionic radius lower than 0.085nm (Menéndez et al., 2007). When huebnerite is crushed, the Mn–O bonds become fractured while tungsten–oxygen bonds remain intact, forming WO_4 and Mn^{2+} interlayers in the direction normal to the (010) plane (Xu et al., 1998).

Figure 7 presents the equilibrium configurations of HA, HOL, HOL–HA and OL⁻–HOL on the huebnerite surface obtained by molecular dynamics simulation. As it was expected (see Fig. 7a and 7b), HA forms five-member ring complex through the two

oxygen atoms of –CONHOH head group with the Mn of huebnerite surface and HOL binds in a bidentate (η^2(O, O)) configuration over all the huebnerite surface (010). In addition to chelate bonding, the –CONHOH head group of HA can form three additional O–H•••O–Mn hydrogen bonds to oxygen in the huebnerite surface and the average O–H distance is 0.228 nm, in contrary, –COOH head group of HOL cannot form hydrogen bonds to bridge oxygen atoms of the huebnerite surface.

As illustrated in Fig. 7c and 7d, both HOL–HA and OL⁻–HOL head groups are bonded closely to the surface and the carbon chains of complexes are highly intertwined to increase the hydrophobic tail-tail bonds. However, head groups of HOL–HA can form four additional hydrogen bonds to the surface, including two hydrogen bonds formed between the –CONHOH head group of HA and the huebnerite surface; two newly generated hydrogen bonds formed between the H of carboxyl head group of HOL and the huebnerite surface where the mean O–H distance is 0.234 nm. Therefore, HOL–HA head groups are more closely attached to the surface than OL⁻–HOL and enforce extra gauche conformations in the backbones resulting in a stronger affinity.
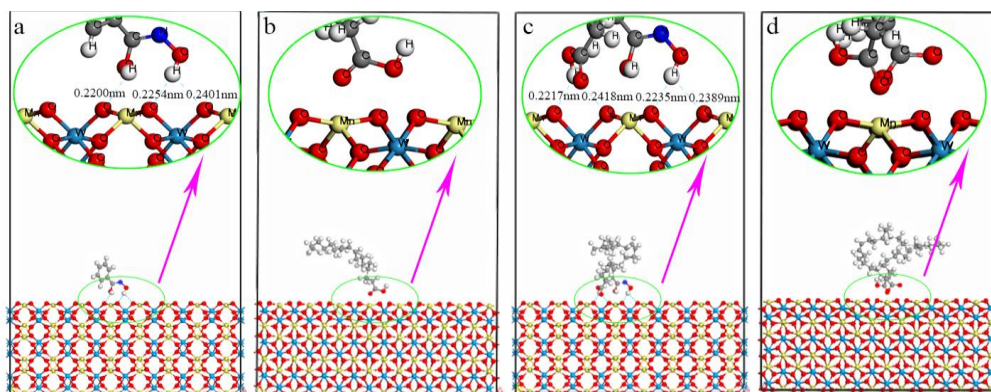

Fig. 7. Equilibrium adsorption configurations of a – HA, b – HOL, c – mixed HA–HOL, d – mixed OL⁻–HOL on the huebnerite surfaces obtained by molecular dynamic simulations

Conclusions

Microflotation of wolframite showed that mixtures of NaOL with BHA of different ratios can improve the recovery of wolframite to varying degrees. The 9:1 NaOL:BHA collector mixture produced the highest wolframite recovery (the improvement over NaOL as a single collector is 21%). Adsorption behaviour of both collectors for NaOL:BHA mixtures of various ratios was also investigated. At ratio of 9:1 or 8:2 (NaOL:BHA), the amounts of NaOL adsorbed were even higher than the amount adsorbed when NaOL was used as the only collector. These results reveal that the

combined use of BHA with NaOL exhibits synergistic effect and the addition of BHA promotes the adsorption behavior of NaOL.

Moreover, MD simulations indicate the formation of HOL–HA complex that can take place spontaneously in NaOL–BHA system. HOL–HA complex more easily interacts with the huebnerite surface (010) than NaOL–HOL (the highest surface active composition in sodium oleate). The head groups of HOL–HA can form four additional hydrogen bonds to the surface which enhance the stability of the adsorption and impose extra gauche conformations. It is therefore concluded that in a binary NaOL–BHA system, the BHA can encourage greater adsorption of the NaOL.

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