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Predicting the efficiencies of 2-mercaptobenzothiazole collectors used as chelating agents in flotation processes: a density-functional study

Abstract In recent years, several new chelating reagents have been synthesized and tested for their collecting power in sulfide and non-sulfide minerals flotation. Many researchers have indicated that chelating reagents have the advantage of offering better selectivity and specificity as flotation collectors. Therefore, density functional theory (DFT) calculations at the B3LYP/6–31G(d,p) level were performed to investigate the observed activities of 2-mercaptobenzothiazole, 6-methyl-2-mercaptobenzothiazole and 6-methoxy-2-mercaptobenzothiazole as the most popular flotation collectors. The molecular properties and activity relationships were determined by the HOMO localizations, the HOMO energies, Mulliken charges and the electrostatic potentials at the thioamide functional group, which is the key site in the forming efficiency of the collectors studied. It is concluded that these quantities can be used successfully for understanding the collecting abilities of 2-mercaptobenzothiazoles. The results obtained theoretically are consistent with the experimental data reported in the literature.

Keywords 2-mercaptobenzothiazole · Flotation · Flotation collectors · Sulfide minerals

Nomenclature

ΔE interaction energies (kcal mol^{-1})
ΔE^{ZPE} zero-point vibrational energy included ΔE values (kcal mol^{-1})
HOMO   the highest occupied molecular orbital energy (eV)
LUMO   the lowest unoccupied molecular orbital energy (eV)
μ dipole moment (D)
r   bond length (Å)
$\angle$ bond angle (^{0})
τ dihedral angle (^{0})

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Introduction

Froth flotation is the single most important process for enriching low grade ores. A variety of surface-active reagents are used in the process, depending on their function which may be as collectors, frothers, depressants and activators. These flotation reagents affect the flotation chemistry in terms of the chemical and electrochemical control of the system. Without the reagents, controlling the wettability of solid surfaces by water, chemistry and electrochemistry of the solution, the dispersing and aggregation of solid particles, and the generation and stability of the froth would not be possible. There are many recent publications in the literature reviewing the development and use of these chemical agents in froth flotation for a better understanding of flotation chemistry [1–5].

The choice of collector type is a very important step in the flotation performance of minerals. In the search for new chemical reagents with strong affinity for certain metal ions, many researchers have indicated that chelating reagents have the advantage of offering better selectivity and specificity as flotation collectors. Therefore, the use of chelating reagents in the flotation process has been paid much attention for many years. Chelating-type collector molecules contain donor atoms such as S, N and O in the functional group, and they are capable of bonding *via* two or more atoms with metal ions in a given mineral to form heterocyclic rings in which the metal atom is one of the members [4]. Since metal-chelates are more stable than ionic or covalently bonded metal salts, chelating-agents are important for the flotation of minerals. The formation of metal complexes with varying stability allows selectivity for the separation of minerals.

Marabini et al. [6] have used a series of new synthetic chelating reagents containing mixed aliphatic-aromatic and alkoxyl-aromatic hydrocarbon chains as collectors. 2-Mer-

captobenzothiazole (MBT) has been suggested as a new collector in the flotation of metal sulfide ores, precious metal ores, tarnished and secondary Cu, Pb and Zn minerals and gold-bearing pyrite [7]. MBT and its derivatives with two possible donor centers (N and exocyclic S atoms) belong to the family of chelating-type collectors. These collector molecules bind surface metal through their N and S atoms and form four-membered rings on the sulfide mineral.

MBT
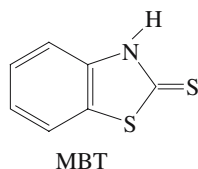
They are found to be alternatives to conventional xanthate collectors, and a lower dosage is required to obtain high recoveries in sulfide-mineral flotation [1, 6].

Marabini et al. [6] have proposed that some structural requisites are essential for the collecting power of molecules, namely: in the benzene ring alkyl or alkoxyl (the alkyl group with oxygen) groups diametrically opposite to the electron-donor heteroatom. Besides MBTs use as collectors, they are also used as bioactive reagents [8] effective corrosion inhibitors [9] and are also used in the synthesis of dyes [10] and polymers [11]. Therefore, knowledge of the structural properties of MBT and its derivatives is valuable information to understand better the chemical reactivity and interaction between the chelating molecule and the surface. The importance of quantum mechanical techniques in studying the electronic and molecular properties of molecules has been well recognized for many years. There have been many modeling studies on collectors in the literature [12, 13]. For this reason, considering of the molecular orbital calculations may be helpful for evaluating the potential use of collectors. Density functional theory (DFT) is developing rapidly as a cost-effective general approach for studying the physical properties of molecules with the feature that a description of electron correlation is included. The objective of this study is to calculate the relevant molecular properties of 2-mercaptobenzothiazole and its 6-methyl and 6-methoxy derivatives as collector using the DFT (B3LYP). These properties are the atomic charges, molecular electrostatic potentials, HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies. The results of this investigation will contribute enormously to understanding the chemistry of this kind of collector molecules.

Materials and methods

The DFT calculations were performed using the B3LYP/6–31G(d,p) [14] level as implemented in the Gaussian 98W program package [15]. The harmonic vibrational frequencies were calculated at the same level of theory in order to identify the local minima as well as to estimate the corresponding zero-point vibrational energy (ZPE). A scaling factor of 0.9804 was used to correct approximately for vibrational harmonicity. Atomic-charge values were determined to describe the reactivity of the molecules and were calculated according to the scheme of Mulliken [16]. The molecular electrostatic potential values at an atomic site can be defined as follows [17]:

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|}$$

Where Z_A is the charge on nucleus A located at R_A. The electrostatic potential $V(\mathbf{r})$ created in the space around a molecule by its nuclei and electrons is well established as a guide to the interactive behavior of molecules, and has been used extensively as a means of identifying molecular regions most susceptible to electrophilic or nucleophilic attack.

Results and discussion

MBT may exist as thione and thiol tautomers, as shown in Fig. 1. The conversion from one tautomeric form to another in heterocycles is important from the point of view of structural chemistry.

A crystallographic study [18] shows that the thione form is predominantly present. The protropic tautomerism of MBT results from the migration of hydrogen from the nitrogen to the exocyclic sulfur atom. Geometrical isomerization can also take place by internal rotation about the C–S bond. The dissociation constant of MBT was found to be $pK_1=7$ by Sutherland [19]. It was proposed that both forms of the molecule may act as collectors depending on the pH-value. With regard to the experimental data, Sandhyarani et al. [20] concluded that MBT adsorbs on Au in the thione form and on Ag in the thiol form. MBT also adsorbs on pyrite and galena in its thione form [1]. On the other hand, reaction mechanisms of MBT and its derivatives with minerals are not fully understood and these mechanisms can be different from those of xanthates. Therefore, a detailed investigation of the relative stability of the various forms of MBT can be important from the point of view of the chemical reactivity of new collectors. In this study, different forms were considered and B3LYP/6–31G(d,p) calculations were performed on the thione and thiol forms.
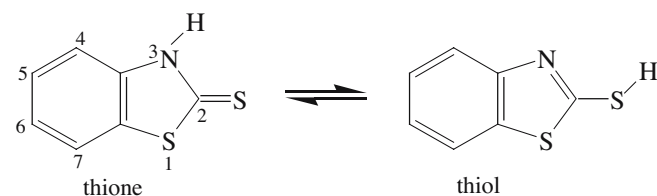

Fig. 1 Schematic representation of the thione–thiol tautomerisim of MBT

Table 1 Selected optimized geometrical parameters

Parameters	Thione			Thiol		
	6-H	6-CH$_3$	6-OCH$_3$	6-H	6-CH$_3$	6-OCH$_3$
r(C2=S)	1.654 (1.662)	1.654	1.655	1.769	1.769	1.770
r(C2–N3)	1.367 (1.353)	1.366	1.364	1.291	1.291	1.290
r(C2–S1)	1.783 (1.732)	1.784	1.787	1.782	1.782	1.785
r(S1–C)	1.763 (1.740)	1.767	1.766	1.759	1.759	1.758
r(N3–C)	1.390 (1.380)	1.391	1.393	1.390	1.389	1.389
∠N3–C2–S1	107.81 (109.2)	107.77	107.67	116.61	116.53	116.34
τ(H–S–C2–S1)	–	–	–	180.0	180.00	180.00

For the numbering of atoms see Fig. 1. Bond distances in Ångström, bond angles in degrees. Experimental values given in parentheses [18]

It has been proposed that 6-alkyl and 6-alkoxyl derivatives of MBT are required for high collecting power [6]. For the sake of simplicity –CH$_3$ and –OCH$_3$ were chosen as the substituents in the phenyl ring. The chemical structures of the compounds studied are very similar. All of the compounds share common structural fragments and they include –CH$_3$ and –OCH$_3$ substituents in the 6-position of the phenyl ring in order to examine the influence of the ring substituents on MBT. Table 1 lists some selected optimized geometrical parameters of the forms studied. The main goal of our work is not a detailed description of the geometrical parameters of the structures. We focused our attention only on the charge distribution, electrostatic potentials and especially localization and energies of the HOMO orbitals. However, we have compared the molecular geometry of MBT calculated using the B3LYP/6–31G(d,p) and X-ray structural data [18]. The theoretical results are in good agreement with the experimental data. As seen from Table 1, the ring parameters of the different forms considered are affected by migration of the hydrogen atom. However, MBT and its derivatives are largely planar molecules.

The relative energies (ΔE) are listed in Table 2 with respect to the energy of the stable thione form. The calculations show that thione tautomers are the most stable forms for all of the compounds studied. The tautomeric preference of the MBT molecule is not affected by inclusion

of –CH$_3$ and –OCH$_3$ groups at position 6. The energy differences between the thiol and thione tautomers are 9.74, 9.72 and 9.38 kcal mol^{-1} for MBT and its 6-CH$_3$ and 6-OCH$_3$ derivatives, respectively. Inclusion of the ZPE correction in the ΔE does not change the tendencies mentioned above. The ΔE value for the 6-OCH$_3$ substituent is the smallest in comparison with the ΔE values obtained for the others.

It is well known that the HOMO and LUMO are often responsible to the reactivities of molecules. They are sometimes collectively termed frontier orbitals because they are molecular orbitals at the energy extremes, and most chemical reactions involve them. The HOMO drawings obtained by GaussView 2.1 [21] are shown in Fig. 2.

The HOMO orbitals were especially taken into account in this study because the collectors examined act as electron-donor species. The HOMO is generally associated with the capacity of a molecule to donate electrons. The HOMO orbitals lie mainly on the N3, C2, S and S1 atoms, except for the 6-CH$_3$ and 6-OCH$_3$ derivatives of the thiol form where HOMO is localized on the N3, C2 and S atoms and on the phenyl ring in the recognition of the active sites preferred for electrophilic attack. Certainly, S1 atoms of the 6-CH$_3$ and 6-OCH$_3$ derivatives of thiol form have no effect on chelate formation with the mineral surface. A metal ion on the mineral surface will usually react with the HOMO of the MBT molecule. There can be several possible ways of

Table 2 Calculated dipole moments (μ, Debye), HOMO (eV) and LUMO (eV) energies, ZPEs (kcal mol^{-1}) and ΔE (kcal mol^{-1}) values

Species	μ	Average Pb recovery, %[b]	HOMO	LUMO	ZPE	ΔE[c]	ΔE^{ZPE}[d]
Thione							
6-H	5.26 (5.2)[a]	30.9	−0.2147	−0.0487	64.85	–	–
6-CH$_3$	5.75	85.0	−0.2107	−0.0456	81.68	–	–
6-OCH$_3$	5.54	85.5	−0.2045	−0.0420	84.81	–	–
Thiol							
6-H	0.99	–	−0.2283	−0.0365	62.54	9.74	7.43
6-CH$_3$	1.49	–	−0.2217	−0.0329	79.37	9.72	7.41
6-OCH$_3$	1.90	–	−0.2098	−0.0275	82.50	9.38	7.07

[a]Experimental value [26]
[b]Experimental value [25]
[c]All ΔE values are relative to the thione form
[d]ΔE values including ZPEs

Fig. 2 HOMO for the different forms of MBT derivatives at an isosurface value of 0.035 au

Thione-6-H

Thiol-6-H

Thione-6-CH$_3$

Thiol-6-CH$_3$

Thione-6-OCH$_3$

Thiol-6-OCH$_3$
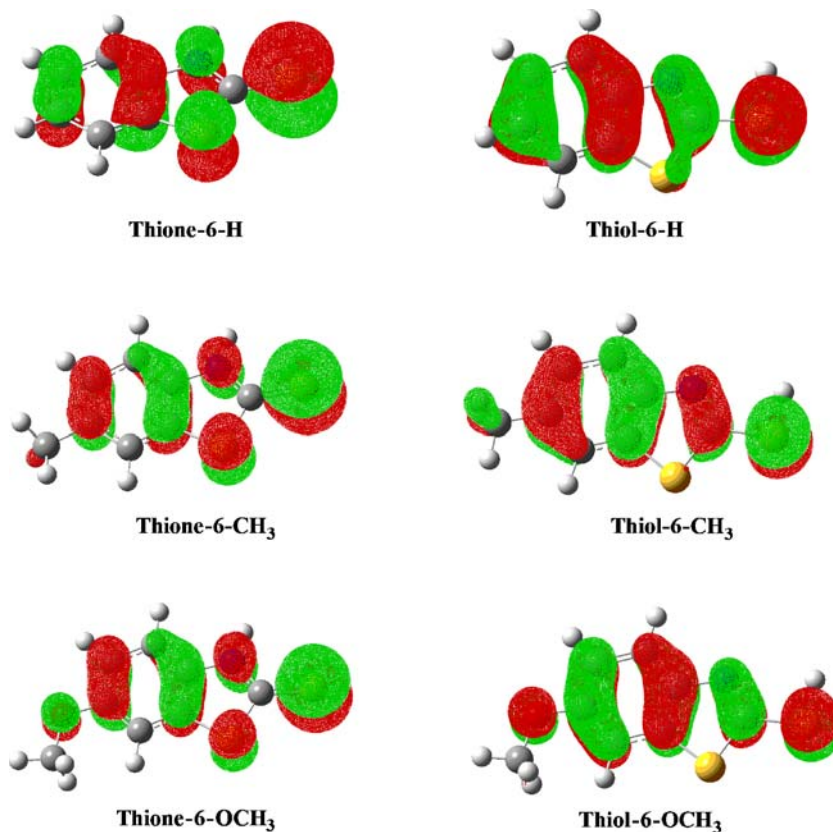
the surface binding via the phenyl ring and the thioamide group (–N–C=S). This is the reason why the benzene ring is essential for the collecting power of MBT and its derivatives. In addition, the results seem to indicate that there is a correlation between the reactivities of MBT derivatives and the HOMO energies. The HOMO energies of MBTs are quite similar. However, comparing the values in Table 2, one can conclude that 6-OCH$_3$ derivatives more nucleophilic than the others. The HOMO energies increase with the change of the substituent from the 6-H to 6-OCH$_3$ derivatives of both forms and imply the highest efficiency for 6-OCH$_3$ with the thione and thiol forms for use as collectors. A similar analysis of MBTs seems to suggest that the thione form is more nucleophilic than the corresponding compound in the thiol form.

Although the HOMO energy is an important factor for the nucleophilic behavior, it is not the ultimate one. The electron density and electrostatic potentials are also fundamental concepts for understanding the chemical reactivity and can explain the phenomena of nucleophilic and electrophilic attack on a molecular system. The chelating ability depends on the electron density on the chelating atoms and in turn is affected by the electronic effects of the substituents in the collector molecule. The atomic charge values obtained by Mulliken population analysis are listed together with the calculated electrostatic potentials in Table 3. Looking at the atomic charges, the –CH$_3$ and the –OCH$_3$ groups at the *para* position of N3 atom on the phenyl ring are able to change the electron density distribution in the thioamide group directly. The electron-withdrawing and electron-releasing properties of groups

Table 3 Calculated Mulliken charges (electrons) and the electrostatic potentials (atomic units)

Species	Mulliken charges				Electrostatic potentials			
	S1	S	C2	N3	S1	S	C2	N3
Thione								
6-H	0.2928	−0.2195	−0.0100	−0.5433	−59.1443	−59.2291	−14.6179	−18.2665
6-CH$_3$	0.2892	−0.2245	−0.0094	−0.5444	−59.1467	−59.2316	−14.6204	−18.2690
6-OCH$_3$	0.2861	−0.2296	−0.0082	−0.5463	−59.1468	−59.2334	−14.6220	−18.2701
Thiol								
6-H	0.2401	0.0635	−0.0761	−0.4476	−59.1484	−59.1571	−14.6356	−18.3494
6-CH$_3$	0.2367	0.0605	−0.0769	−0.4491	−59.1507	−59.1592	−14.6386	−18.3517
6-OCH$_3$	0.2326	0.0573	−0.0778	−0.4500	−59.1511	−59.160	−14.6410	−18.3526

occur on the basis of two factors: inductive and resonance effects. In addition, as the substituents are in a conjugated position, it is commonly accepted that the interaction by resonance effects is considered to be more important than the inductive effects. The inductive effect of the methoxyl group, $-OCH_3$ makes it slightly electron withdrawing. Oxygen, as we know, is more electronegative than carbon. The resonance effect of the $-OCH_3$ group is far more important than its inductive effect, and this resonance effect makes the $-OCH_3$ group electron-releasing. The $-CH_3$ group can be considered as electron-releasing. However, the methoxyl group has more powerful electron-releasing ability than $-CH_3$. Additionally, Taft's substituent constant (σ^*) for $-OCH_3$, which is used to describe electronic effects, is -0.22, implying high electron releasing power relative to $-CH_3$ [22]. This means that $-OCH_3$ will create higher electron density on the atoms of the thioamide group than $-CH_3$. For the compounds examined, it is possible to observe that the N3 and S atoms for the thione form and the N3 atom for the thiol form present a considerable excess of negative charge, and S1 atoms present positive charges for all species of the two forms studied. Because most of the electron density of the S1 atom is delocalized by resonance with the aromatic ring making it poor donor atom. Woods et al. [23] investigated interaction of the sulfide mineral flotation collector, MBT, with silver, copper and gold surfaces by surface enhanced Raman scattering (SERS) spectroscopy. The attachment to the surface is between the surface metal atoms and the exocyclic sulfur atom of MBT instead of the S1 atom. This result indicates that the S1 atom is probably positively charged and is not included in bonding between the metal atoms and the MBT collector. Therefore, the results obtained confirm the experimental data obtained by Woods et al. [23]. As a result, especially the N3 and S atoms in the thione, and the N3 atom in the thiol can be identified as the favorable reactive sites for metal-atom attack.

The theoretically estimated electrostatic potentials of the thioamide group, which is the chelating part of the molecule, also provide a quantitative description of the activity of the MBTs to form chelates with the metal atom on the mineral surface. As can be seen from Table 3, the absolute values of the electrostatic potentials at the sites of the chelating group increase on going from the 6-H to the 6-OCH$_3$ for the thione and thiol forms. The results indicate that there is a correlation between the electrostatic potentials and activities of MBT derivatives.

On comparison, it can be seen that theoretically obtained results about the activity of MBTs in this study are in good agreement with experimental results. For example, Contini et al. [24] carried out an infrared study on MBT and two of its derivatives (6-CH$_3$ and 6-OCH$_3$) adsorbed on the PbS (galena) surface. They concluded that in the case of MBT on PbS, the peaks of the adsorbed complex are rather low and difficult to detect. The amount adsorbed slightly increases in the case of the 6-CH$_3$ substituent compared with MBT, and attains a maximum with 6-OCH$_3$. This means that with the $-OCH_3$ substituent in position 6, the

adsorption and the collecting ability of MBT reaches a maximum [6]. Additionally, Barbaro and Piga [25] adopted various derivatives of MBT (6-nC$_3$H$_7$ and 6-nOC$_3$H$_7$) in the flotation of lead and zinc minerals to evaluate the Pb–Zn selectivity. The study indicated that the selectivity of the collectors was related to their molecular structure. The average Pb recovery in percent is found to be 30.9, 85.0 and 85.5 for MBT and its 6-nC$_3$H$_7$ and 6-nOC$_3$H$_7$ derivatives, respectively. These ratios show the difference in the collector selectivity, and an alkyl and alkoxyl groups are necessary to ensure the collecting power of MBT.

Conclusions

This theoretical study on MBT and two of its derivatives indicated that the selectivity of collectors is a function of the structure and nature of the functional group present. According to the HOMO localizations, we found two regions, the phenyl ring and thioamide group, that play a key role in the activity of MBTs. While the phenyl ring plays an important role in the interaction with mineral surface, the thioamide group is particularly important in the activity of the compounds considered here. The value of the HOMO energies shows the best efficiency for 6-OCH$_3$ derivative when being used as collector. The calculated Mulliken charges indicate that thioamide group presents a considerable excess of negative charge and is the most favorable site for the metal atom attack. The $-OCH_3$ group is a stronger electron donor than $-CH_3$, resulting in an increase in the electron density of the related atoms and thus in the reactivity of the compounds as a nucleophile.

As a result, the following collecting ability order was theoretically obtained: 6-OCH$_3$ >6-CH$_3$ >6-H derivatives of MBT, consistent with the experimental results.

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