

# Molecular Modeling as an Approach for Flotation Reagents Selection

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**Abstract:** *In the present study computational modeling of minerals and reagents was performed using Chem Bio 3D and ChemOffice2005 by Cambridge Soft with optimization by MM2. The semi empirical calculations were provided by MOPAC. Molecular structures of antimony clusters were created. DTF approach was used to determine energies such as HOMO, LUMO and SOMO. Absolute hardness  $\eta$  and chemical potential  $\chi$  by Pearson and Parr have been calculated. The strategy of prognosis of collector activity evaluation (PCAE) has been proposed as a consistent approach to estimate the interaction between a collector and a mineral cluster as a difference of total energy and sum of cluster energy and collector energy. To improve the separation of minerals the method of complex formation between collectors and mineral clusters was harnessed. The probable increasing collecting ability of sulfhydryl collectors for stibnite follows the order as : butyl xanthic acid (BXA), dimethyldithiocarbamic acid (DMDTCA), piperidine dithiocarbamic acid (PDTCA), mixture of butyl xanthic acid and dithiocarbamic acid (BXA+DTCA), Bis(2-(dibutylamino)ethyl) dithiophosphonic acid (DBAEDTPA) and diethyl aminoethylxanthic acid (DEAEXA). Dialkylamino sulfhydryl collectors can be considered as prospective reagents for stibnite ore flotation. The results obtained were confirmed by experimental data in ore flotation.*

**Keywords:** Flotation, Mineral Clusters, Molecular Modeling, Collector Activity Evaluation

## 1. Introduction

Several millions organic compounds with various structure have been synthesized over the past 20 years. Several thousands of chemicals were either tested or suggested as flotation reagents. Nowadays there are only a few hundred of these reagents that are extensively used in flotation. Sulfur-containing reagents are widespread collectors for sulfide minerals recovering. The representation of sulfhydryl collectors that has been extensively studied, are xanthates, dithiophosphates and dithiocarbamates, although their derivatives are equally important [1]. Xanthates as powerful collectors are commonly used for flotation of sulfide minerals such as chalcopyrite, galena, sphalerite, stibnite and etc. Dithiophosphates are weaker but more selective than xanthates [1] - [5]. Dithiocarbamates have a high specificity for antimony minerals [1], [6].

Although all of these compounds contain sulfur, the structure of molecules is rather different. This is the connection between the spatial structure of molecules and chemical activity of the compounds. The flotation performance of these collectors have been investigated related on their functional groups. Moreover each compound has its special physico-chemical properties. Therefore the most troublesome question for researchers remains the estimation of quantitative structure-property relationship. The knowledge generated in these studies is extremely helpful in quick selection of collectors with desired properties as well as in designing of new reagents schemes. The correlation established can allow to determine the direction of synthesis of new compounds which could play the key role as collectors for sulfide flotation.

## 2. Computational Modeling

There are a fairly large number of approaches to choose the flotation reagents with definite properties [7]. The approach for reagent selection is based on the consideration of more than just the chemistry of one reagent in isolation or more than just one type of reagent for a given mineralogy. In fact, all the chemical and operational factors are considered simultaneously. The preference of using of chemical programs and computer technologies appears to be at the significant value [8], [9].

Stereochemical representations of mineral and reagent molecules play the significant role in explanation of their behavior in flotation. Goal of computational chemistry is to mathematically represent the chemical reality. Modern computational methods allow to find the way of visualizing a three-dimensional model of the molecule and to understand the connection between the spatial structure of the molecule and physical properties of the substance as well as its chemical activity [7], [10].

First principle density functional theory (DFT) method offers an effective tool in the calculation of the properties and energies of the various collectors [11]-[17]. DFT study is used to determine the optimal molecular structure and calculate atomic charge values, the compositions and energies of HOMO and LUMO of sulfhydryl collectors. The theoretical methodology established and results obtained provide an atomic level understanding on interactions and bond formation mechanisms between collector molecules and sulfide mineral surfaces [17].

Flotation reagents selection takes years to discover a new reagent and it is very costly. Therefore our goal was to cut

down the research time by reducing laboratory experiment using computer modeling and docking approach.

### 3. Research Objectives

The objectives of the present study are antimony minerals and thiol collectors which are used in practice for stibnite flotation from Sb-Hg,Sb-As ores at Djijicrut deposit (Tadjikistan) and Sarilah Mineral Processing Plant (Yakutia, Russia) . These collectors have been established as standard reagents for estimation the effectiveness of organic compounds studied.

### 4. Methods

#### 4.1 Computational Methods

In the present study computational modeling of minerals and reagents was performed using Chem Bio 3D and ChemOffice2005 by Cambridge Soft with optimization by MM2. MM2 energy-minimization is used to prevent a freely rotatable bond and calculate properties of organic molecular models. The semi empirical calculations were provided by MOPAC.

#### 4.2 Docking Approach

Complex formation have been established with the aid of computational docking technique. The docking method is a search algorithm and a scoring function that predicts the preferable orientation of one molecule to a second to form a stable complex and estimate collecting activity of reagents. The approach has proved useful in identifying relevant candidates for several flotation applications [18].

### 5. Results and Discussion

#### 5.1. Molecular Models of Mineral Clusters

The strategy of evaluation has been proposed as an approach to make a choice of organic compounds as a prospective collectors in stibnite flotation. Possessing the high chemical activity the organic compounds studied can show the stronger complexing properties comparing to the other collectors because of the presence of the functional group of thione and thiol sulfur atoms having donor properties. The characteristics of flotation reagents and organic compounds studied are provided in Table 1.

Table 1 contains the information about chemical formulas, molecular weights and chemical analysis data for various organic compounds where 1-Butyl xanthic acid(BXA); 2-Dimethyldithiocarbamic acid (DMDTCA); 3-Diethylaminethylxanthic acid (DEAEXA); 4-Piperidinedithiocarbamic acid (PDTCA); 5-Bis (2-(dibutylamino) ethyl) dithiophosphonic acid(DBAEDTPA); 6-Quinolinethiol(QT);7-Tetrazol;8-O,OdibutylS-(2-mercaptoethyl) phosphorodithioate (DBMEDTPA).

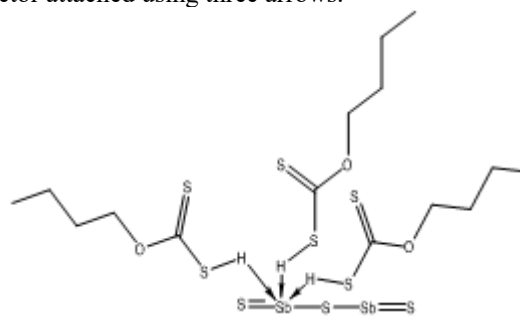
**Table 1:** Samples characteristics

N	Chemical formula	Mol. weight (g)	Elemental analysis
1	C <sub>3</sub> H <sub>10</sub> OS <sub>2</sub>	150	C40.0;H6.67;O10.67;S42.6
2	C <sub>3</sub> H <sub>7</sub> NS <sub>2</sub>	121	C29.75;H5.78; N11.57;S52.90
3	C <sub>7</sub> H <sub>15</sub> NOS <sub>2</sub>	193	C43.49;H7.82;N7.24;O8.28;S33.17
4	C <sub>6</sub> H <sub>11</sub> NS <sub>2</sub>	161	C44.68;H6.87;N8.68;S39.76
5	C <sub>20</sub> H <sub>45</sub> N <sub>2</sub> PS <sub>2</sub>	408	C58.78;H11.10; N6.85;P7.58;S15.69
6	C <sub>9</sub> H <sub>7</sub> NS	161	C67.08;H4.35; N8.69;S19.88
7	C <sub>7</sub> H <sub>6</sub> N <sub>4</sub> S	178	C47.19;H3.37;N31.46;S17.98
8	C <sub>10</sub> H <sub>23</sub> O <sub>2</sub> PS <sub>3</sub>	302	C39.71;H7.66;O10.58;P10.24;S42.66

The stibnite cluster activated has been presented as a formula PbSb<sub>2</sub>S<sub>4</sub> (PbS Sb<sub>2</sub>S<sub>3</sub>) based on the special studies. Molecular structures of mineral-collector clusters were created. DTF approach was used to determine energies such as HOMO, LUMO and SOMO. Absolute hardness  $\eta$  and chemical potential  $\chi$  by Pearson and Parr have been calculated.

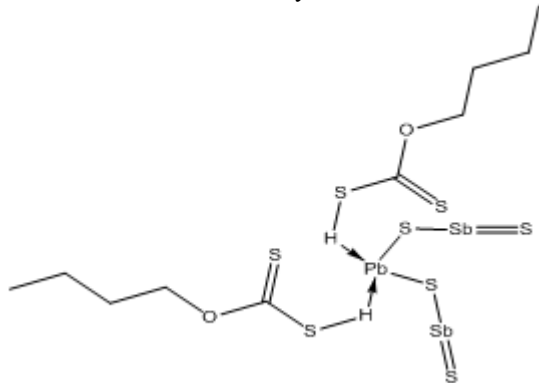
The strategy of prognosis of collector activity evaluation (Pcae) has been proposed as a consistent approach to estimate the interaction between a collector and a mineral cluster as a difference of total energy and sum of cluster energy and collector energy.

The chemical reaction between a thiol collector and a sulfide mineral is a frontier-controlled reaction [15], [16], [19], [20], i.e. a thiol collector transfers its HOMO electrons to a metal atom on the sulfide mineral surface to form a normal covalent bond. Additionally, if a metal atom on the sulfide mineral surface has richly d-orbital electrons and a thiol collector has the electron-accepting ability, the metal atom can transfer some of its d-orbital electrons to the LUMO of the thiol collector to form back donation covalent bonds. The complex of the stibnite cluster with three molecules of butyl xanthate attached to antimony atom is shown in Figure 1. In case of stibnite the atom of antimony has oxidation number equal to three therefore Figure 1 indicates the collector attached using three arrows.



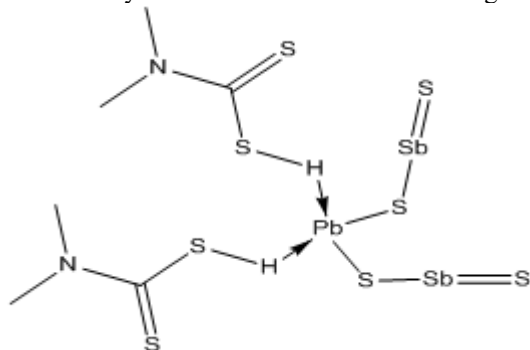
**Figure 1:** Complex of stibnite cluster with 3 molecules of butyl xanthate attaching to antimony atom.

Figure 2 represents the similar complex but for stibnite activated by  $Pb^{2+}$  cations. As arrows indicate lead cation is attached to two molecules of butyl xanthate.



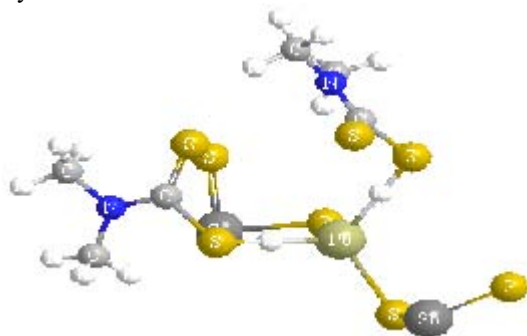
**Figure 2:** Complex of stibnite cluster with 2 molecules of butyl xanthate attaching to lead atom.

Additionally, the complex of stibnite cluster activated by  $Pb^{2+}$  with dimethyldithio carbamate is shown in Figure 3.



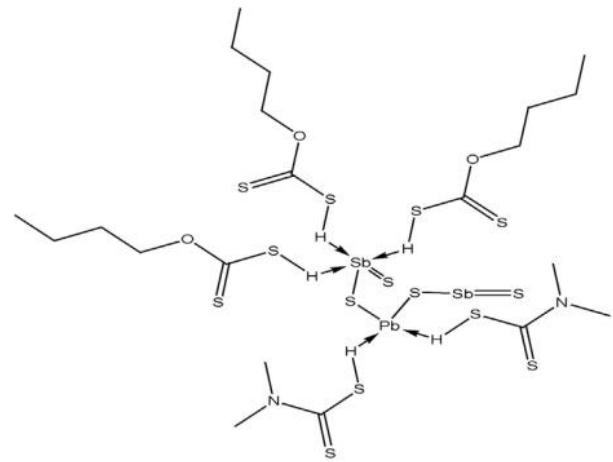
**Figure 3:** Complex of stibnite cluster with 2 molecules of DMDTC attaching to lead atom

Figure 4 represent the optimal geometrical model of the complex of stibnite cluster activated by  $Pb^{2+}$  with dimethyldithio carbamate.



**Figure 4:** 3D model of the complex of stibnite cluster with 2 molecules of DMDTC attaching to lead atom .

The optimized geometrical model of activated stibnite cluster with the combination of butyl xanthate and dimethyldithiocarbamate was created. This model represents the real flotation process with the mixture of collectors such as BX and DMDTC. Figure 5 shows the complex of activated stibnite attaching to three molecules of BX by antimony atom and to two molecules of DMDTC by lead atom.



**Figure 5:** Complex of activated stibnite attaching to three molecules of BX by antimony atom and to two molecules of DMDTC by lead atom.

## 5.2. Prognosis of Collector Activity Evaluation (PCAE)

Models given in Figure 1-5 have been taken into account to calculate the physico-chemical constants for collectors. The strategy of collector activity evaluation has been proposed as a consistent approach to estimate the interaction between a collector and a mineral cluster as a difference of total energy and sum of cluster energy and collector energy [21]-[23].

$$E = E_{\text{complex}} - (E_{\text{cluster}} + E_{\text{collector}}), \text{ eV(1)}$$

The lower PCAE the stronger the ability of the collector to interact with the mineral cluster. The calculated PCAE for various mineral clusters and collectors such as BXA, DMDTCA and the mixture of them are given in Table 2.

**Table 2:** Calculated PCAE (eV)

Mineral cluster	PCAE, eV		
	BXA	DMDTCA	BXA+ DMDTCA
$Sb_2S_3$	-0.5491	-0.6871	
$PbSb_2S_4$	-1.1517	-1.6756	-1.8463

According to Table 2 the decrease of prognosis of collector activity evaluation (PCAE) for stibnite activated is in the following order: BXA (-1,1517), DMDTCA (-1,6756), BXA+DMDTCA(-1,8463). From the relevant studies conducting on flotation it can concluded that floatability of stibnite is changing in reverse order to PCAE. Based on this order the stibnite floatability is increasing from the individual collector up to the mixture. As a matter of fact, the lower PCAE the higher floatability of stibnite. The lowest magnitude of PCAE obtained for the mixture of BXA and DMDTCA is related to the maximum recovery of stibnite.

The theoretical knowledge obtained from research on PCAE provided a basis for the industrial flotation testing of stibnite by the combination of BX and DMDTC from Sb-Hg, Sb-As sulfide ores on Sarilah Mineral Processing Plant (Yakutia, Russia). The antimony ore with the grade of 15,6-14,91% Sb and 0,33-0,21% As was processed in differential flotation circuit in which antimony is recovered to a

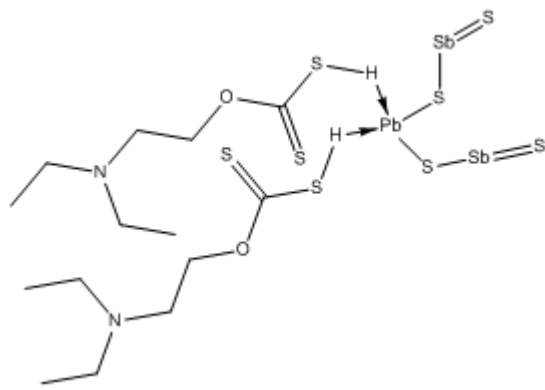
concentrate at a grade of 62,39-59,20% Sb, 0,43-0,36% As, leading tailings containing 1,73-1,13% Sb and 0,33-0,21% As.

Furthermore on the base of computer modeling it was suggested the range of organic compounds which properties as proposal collectors were predicted. Table 3 contains a PCAE data for stibnite clusters and various reagents with amino group.

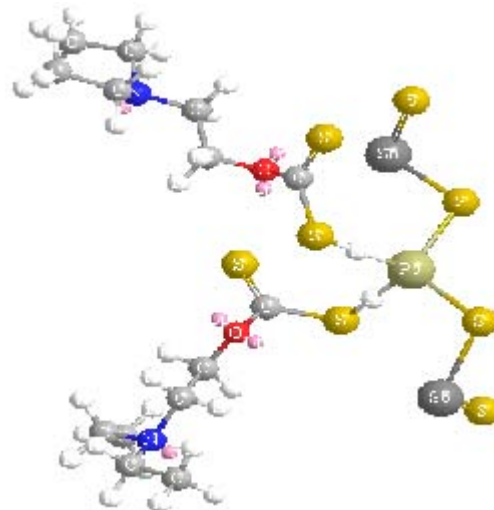
**Table 3:** Calculated PCAE (eV)

Reagents	Mineral Cluster	PCAE,eV
Tetrazol	PbSb <sub>2</sub> S <sub>4</sub>	-1.1846
DBMEDTPA	PbSb <sub>2</sub> S <sub>4</sub>	-1.0846
QT	PbSb <sub>2</sub> S <sub>4</sub>	-1.5104
PDTCA	PbSb <sub>2</sub> S <sub>4</sub>	-1.7696
DBAEDTPA	PbSb <sub>2</sub> S <sub>4</sub>	-8.0223
DEAEXA	PbSb <sub>2</sub> S <sub>4</sub>	-602.3262

The results indicate that the difference in PCAE for some derivatives and BXA does not have the significant value while the complex of stibnite with DEAEXA has PCAE of -602,3262 eV . Comparing this with the PCAE data for stibnite activated and BXA, a significant decrease in PCAE for DEAEXA from -1,1517 ( BXA) to -602,3262 can be seen and from the previous discussion it is evident that this reagent can be considered as the most perspective collector for stibnite flotation. The complex of DEAEXA with stibnite activated is shown in Figure 6 and its optimized geometrical structure presents in Figure 7.



**Figure 6:** The complex of DEAEXA with stibnite activated Pb<sup>2+</sup>



**Figure 7:** Optimized geometrical structure of the complex of DEAEXA with stibnite activated.

## 6. Future Scope and Implications of the Study

Computational modeling can find a molecular which would be expected to interact with a mineral cluster. This is the best way to predict the structure of the intermolecular complex formed between a mineral and a collector to forecast the prospective reagents for flotation operations.

## 7. Conclusion

The computational method can be directly applied as a tool in investigation of surface-collector interaction. The theoretical knowledge obtained from research on mineral-collector clusters provided a basis for the stibnite flotation from Sb-Hg and Sb-As ores with the combination of BX and DMDTC.

The values of PCAE for stibnite clusters with sulfhydryl collectors have been calculated. It has been established that PCAE was decreased in order of: butyl xanthic acid (BXA), dimethyldithiocarbamic acid (DMDTCA), piperidine dithiocarbamic acid (PDTCA), mixture of butyl xanthic acid and dithiocarbamic acid (BXA+DTCA), Bis(2-(dibutylamino)ethyl) dithiophosphonic acid (DBAEDTPA) and diethyl aminoethylxanthic acid (DEAEXA). The flotability of stibnite is changing in reverse order comparing to PCAE. There is a strengthening effect of amino group in collectors on flotability of stibnite therefore dialkylamino sulfhydryl collectors can be considered to be prospective reagents for sulfide antimony ore flotation.

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## Author Profile



**Olga Ibragimova** received the MS degree in Mineral Processing Engineering from the Moscow Institute of Steel and Alloys, Russia in 1986. During 1986-1994 she stayed in Ore Dressing Laboratory, Institute of Chemistry, Tajik Academy of Science to study the phenomenon of the effect of combination of sulfur-containing collectors on non-ferrous ores flotation using spectroscopic methods. Then she has been an associate professor at the Samara State Technical University, Russia, over the past 15 years. Presently, she is teaching at the University of Dodoma, Tanzania. Current research interests include Computer Modeling of Chemical Compounds and Processes.