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# Theoretical studies on the interaction of anionic collectors with $Cu^{+}$, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ ions

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**Abstract.** The influence of collector structure on interaction with metal cations was modelled by computational ab initio methods. The interaction energies were calculated between metal ions ($Cu^{+}$, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$) and selected collector anions: ethyl xanthate, ethyl trithiocarbonate, dithiobutyric acid, ethyl dithiocarbamate, diethyl dithiocarbamate, diethylphosphinecarbodithioic acid and diethoxyphosphinecar bodithioic acid. The strongest interaction was found with diethyl dithiocarbamate. The results give qualitative information on the effect of the collector structure on the initial adsorption steps on sulphide mineral flotation.

**Key words:** Ab initio quantum chemical methods and calculations – Zinc – Copper – Lead – Ethyl xanthate

## 1 Introduction

Froth flotation is a commonly employed process for the separation of minerals from their ores. Valuable minerals are separated from the crude ore with the help of organic chemicals known as collectors. These chemicals induce differences in the hydrophobicity of the mineral surfaces and facilitate the attachment of the minerals to air bubbles. The desired mineral particles are then collected with the froth [1]. Thiols, such as alkyl xanthates, are regularly used as collector molecules in the flotation of sulphide minerals [2, 3, 4]. Although effective in the recovery they are also unselective. The flotation result can be improved through the use of more selective collectors in addition to xanthates. Furthermore, chemicals such as activators, depressants and pH regulators can be added to the flotation slurry to influence the concentration of the target mineral [5, 6].

Sphalerite (ZnS), the most important mineral of zinc [7], always coexists with copper and lead sulphide minerals [5]. Since the sphalerite surface is less easily oxidized than galena (PbS) and covellite (CuS), its flotation properties are different. Zinc sulphide can be effectively flotated through activation with copper(II) ions [8].

Several kinds of interactions may occur between the sulphide mineral surface and the chelating agents: chemisorption, physisorption, formation and, under suitable conditions, precipitation of a metal collector salt, and oxidation of the collector to dithiolate (e.g. xanthate to dixanthogen), which is then adsorbed on the surface [7, 9]. Our objective was to find out how the structure of a thiol collector influences its interaction with the metal cations $Cu^{+}$, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$. By this we aim to get qualitative information on the differences in the initial adsorption process. The basic knowledge of the structural dependencies would help in tailoring suitable collectors for sulphide mineral flotation.

The thiol collectors that were studied differ in the number of hydrocarbon chains and in the type of atom or group directly attached to the $CS_2^-$ group. Although they are not used in normal sulphide mineral flotation, diethylphosphinecarbodithioic acid [$(CH_3CH_2)_2PCS_2^-$], diethoxyphosphinecarbodithioic acid [$(CH_3CH_2O)_2PCS_2^-$] and dithiobutyric acid ($CH_3CH_2CH_2CS_2^-$) were included in the study to explore the possibility of modifying the thiol collectors so that the interaction between the collector and the transition-metal or heavy-metal ions would be maximized.

## 2 Computational methods

Computational methods offer an effective way to study the interactions between collector molecules and metal ions such as Cu(I), Cu(II), Zn(II) and Pb(II). Information about the strength of the interaction is difficult to obtain experimentally, since the overall flotation mechanism comprises many surface processes and is highly complex.

All the calculations were made with the Gaussian94 program [10] and the energies were corrected with the

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full counterpoise technique [11]. The calculations were made at the Hartree–Fock (HF) level of theory and with the MP2 [12] and the B3PW91 methods [13, 14]. The basis sets used can be seen in Tables 1 and 2.

Relativistic effects can be important when calculating the interaction energies for the heavy metals. For the first-row transition metals the relativistic effects are usually minor compared to other computational errors, but for heavier elements, like Pb, the relativistic effects should be taken into account. To test this, we calculated the interaction energy of ethyl xanthate to Pb$^{2+}$ ion using the quasi-relativistic effective-core potential basis set (Stuttgart RLC ECP) for the Pb$^{2+}$ ion [15].[1] For the Pb(II) oxidation state, relativistic effects were found to be small. For example, with the B3PW91/Huz/6-31G*//HF/Huz/3-21G* and B3PW91/ECP/6-31G*//HF/ECP/3-21G* methods the interaction energies were −1463 and −1453 kJ/mol, respectively. Therefore, the succeeding calculations with the other collector structures were performed with Huzinaga's all-electron basis set for all the metal ions.

Because, for example, xanthates are usually bidentately coordinated in the metal complexes [16], the calculations were carried out with both sulphur atoms bonding to the metal (Fig. 1). The geometries of the complexes were fully optimized.

## 3 Results and discussion

### 3.1 Choice of the method

Because of the lack of information about the interaction energies and the structures formed between the collector and the metal ion, the method of calculation was chosen by comparing the results for the ethyl xanthate–metal complexes obtained at the HF level of theory and with the more sophisticated MP2 [12] and nonlocal hybrid functional B3PW91 methods [13, 14].

Selected geometrical parameters of the fully optimized zinc ethyl xanthate complex (Fig. 1) calculated at different levels of theory and the experimental values [17] of the same parameters are shown in Table 1. Although the experimental parameters were collected from solid zinc ethyl xanthate with bridging sulphur atoms bonded to two zinc atoms, we can use these as qualitative guidance when comparing different methods. Extra information about the experimental structural parameters can be found from the zinc(II) bis(*O*-butyldithiocarbonate) complex [18], which has both bridging and chelating xanthate ligands. In the chelating ligands the S–Zn distances are 2.383 and 2.375 Å. From the latter experimental values we can see that

**Table 1.** Selected geometrical parameters of the zinc ethyl xanthate complex model. The calculations were full geometry optimizations. Experimental values were taken from the crystal structure of the solid zinc ethyl xanthate [17]

| | HF/Huz/3-21G*[a] | HF/3-21G* | HF/6-31G*[b] | MP2/6-31G*[b] | B3PW91/Huz/3-21G*[a] | B3PW91/Huz/6-31G*[a] | Experiment [17] |
|---|---|---|---|---|---|---|---|
| Bond length (Å) | | | | | | | |
| C4–S6 | 1.743 | 1.743 | 1.747 | 1.742 | 1.756 | 1.758 | 1.61–1.70 |
| C4–S5 | 1.743 | 1.745 | 1.748 | 1.746 | 1.757 | 1.758 | 1.61–1.70 |
| S5–Zn | 2.228 | 2.228 | 2.259 | 2.217 | 2.141 | 2.128 | 2.337–2.369 |
| S6–Zn | 2.248 | 2.251 | 2.282 | 2.239 | 2.159 | 2.145 | 2.337–2.369 |
| C4–O3 | 1.276 | 1.277 | 1.253 | 1.293 | 1.304 | 1.278 | 1.33–1.42 |
| O3–C2 | 1.512 | 1.511 | 1.474 | 1.491 | 1.525 | 1.48 | 1.50–1.51 |
| Binding angle (degrees) | | | | | | | |
| S6–C4–S5 | 123 | 123 | 121 | 123 | 125 | 124 | 123–128 |

[a] Huzinaga split valence basis set with polarization functions for zinc [19]. The basis set for zinc was (43211/421*/21)

[b] Basis sets for zinc, see Ref. [20]

**Table 2.** Basis set superposition error (*BSSE*) corrected interaction energies (kJ/mol) between various metals and the ethyl xanthate molecule calculated at different levels of theory

| | HF/3-21G* | HF/Huz/3-21G*[a] | HF/6-31G*[b] | MP2/6-31G*[b] | B3PW91/Huz/3-21G*[a] | B3PW91/Huz/6-31G*[a] | B3PW91/Huz/6-31G*//HF/Huz/3-21G*[c] |
|---|---|---|---|---|---|---|---|
| Cu(I) | −505 | −573 | −619 | −663 | −677 | −687 | −721 |
| Cu(II) | −1516 | −1528 | −1631 | −1719 | −1775 | −1788 | −1785 |
| Zn(II) | −1544 | −1544 | −1631 | −1693 | −1647 | −1662 | −1685 |
| Pb(II) | [d] | −1368 | [d] | [d] | −1458 | −1466 | −1463 |

[a] Huzinaga split valence basis set with polarization functions for metals [19]. The basis set for zinc was (43211/421*/21), for copper (43211/421*/21) and for lead (4322211/422211/4221*/3)

[b] Basis sets for copper and zinc, see Ref. [20]

[c] Geometry optimization performed with the HF/Huz/3-21G* method and energy calculation performed with the B3PW91/Huz/6-31G* method

[d] No standard basis set

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[1] The basis set was obtained from the Extensible Computational Chemistry Environment Basis Set Database, version 9/12/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA. Contact David Feller or Karen Schuchardt for further information

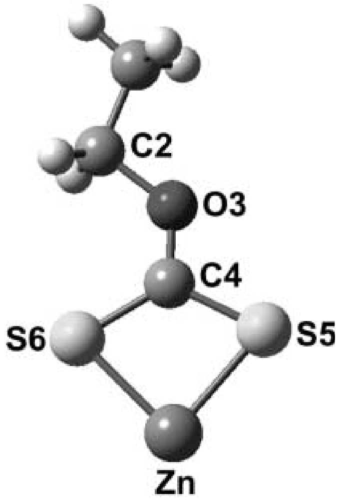

**Fig. 1.** Geometry-optimized structure of the zinc ethyl xanthate complex

alkyl xanthates can also form chelating complexes with zinc and the bonding distances vary depending on the environment. According to our calculations, the carbon–sulphur distances are slightly overestimated with all methods, while the metal–sulphur distances are underestimated. In all cases, however, the HF methods gave comparable values to the more sophisticated methods.

The basis set superposition error (BSSE) corrected interaction energies calculated by the different methods are compared in Table 2. The difference in the interaction energies between Cu(II) and the ethyl xanthate ligand and Zn(II) and the ethyl xanthate ligand is reversed in sign upon going from HF methods to MP2 and density functional theory (DFT) methods. The DFT method gives a larger energy difference than the MP2 method, but the order is the same. Furthermore, the differences to the Cu(I) and Pb(II) ethyl xanthate interaction energies are so large that all the systems would produce the correct energy order.

A compromise was required between the accuracy of the geometrical parameters and the level of theory because this approach will later be applied to the surfaces of sulphide minerals. The MP2 method is not feasible for larger systems. The DFT method gives slightly less accurate geometry (Table 1) and it converges slowly. Inspection of the results for the zinc ethyl xanthate complex shows that successful geometry optimizations were carried out with the computationally less demanding HF/Huz/3-21G* method, while the interaction energies were calculated with the B3PW91/Huz/6-31G* method. Together these methods allow a qualitative comparison of different collectors and give information on the basic properties of the interaction between collector molecules and metal cations.

The solvent effects were not taken into account in this study because this preliminary research will be expanded to surfaces. For surfaces, the use of continuum solvation methods or the supermolecule approach using ab initio methods will not be straightforward. Although the solvent effects are neglected we can get qualitative information about the influence of the collector structure on the interaction with different metal cations.

### *3.2 Interactions of collectors and metals*

The thiol collectors (S–S type) act like chelate-forming reagents with the dissolved metal ions or the surface metal cations on the surfaces of copper sulphide minerals such as covellite (CuS) [21]. The thiol group usually acts as a bidentate ligand in metal complexes [16], and we may predict that the same situation applies to sphalerite (ZnS) and galena (PbS).

Preliminary studies on the interaction of different collector molecules with sulphide minerals were carried out with separate $Cu^{+}$, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ ions. Both $Cu^{+}$ and $Cu^{2+}$ cations were chosen, because, for example, in the zinc sulphide flotation, the Cu(II) ion can change its oxidation state to Cu(I) to form copper(I) ethyl xanthate [8].

The calculations are relatively fast, but with the disadvantage that neither the environment nor the influence of the formation of other complexes on the mineral surface is taken into account. This will lead to an overestimation of the interaction energies. Furthermore, the system does not take into account the effect of neighbouring metal atoms, which could lead to a different kind of adsorption mechanism on the mineral surface. The study of the basic properties of the interactions between selected metals and collectors can, nevertheless, be initiated with a simple system and can then be expanded to surfaces.

The effect of different functional groups on the interaction energies was studied by replacing the ethoxy tail (EO–) of the ethyl xanthate molecule with the ES, $ECH_2$, ENH, $E_2N$, $E_2P$ and $(EO)_2P$ groups (E = ethyl) (Fig. 2). The purpose behind these choices was to study the electronic effects on the interaction energies and charge distributions. This was expected to help in explaining the properties of the collector molecules and then designing more effective collectors. The effect of the conformation of the hydrocarbon tail on the interaction energies was diminished by choosing similar structures for all the collectors. A full conformational analysis was not performed since the influence of the ethyl groups was found to be negligible in test calculations. The BSSE-corrected interaction energies are set out in Table 3. Although the energies are high, partly owing to direct ion–ion interaction and the lack of solvent molecules, we can draw conclusions about the influence of the different collector structures.

As can be seen in Table 3, the interaction energies are largest for the complexes of $E_2N$ with all the metals. Since the ENH–metal complexes also exhibit larger interaction energies than the complexes with other collectors, we can conclude that the nitrogen atom influences the collector properties when it is bonded directly to the $CS_2^-$ group. According to the literature, dithiocarbamates are stronger collectors than xanthates [22]. In microflotation studies on malachite $[Cu_2(CO_3)(OH)_2]$, for example, monoalkyldithiocarbamates have proven to be more effective in recovery than

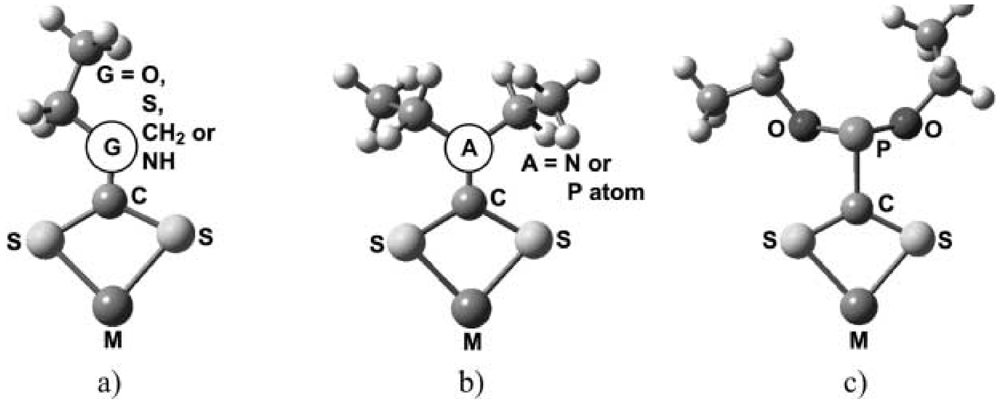

**Fig. 2.** **a** Chelate structure of metal ethyl thiol complex model ($M$ = Cu, Zn or Pb atom, $G$ = O, $CH_2$, S or NH group). **b** Chelate structure of metal diethyl thiol complex model ($M$ = Cu, Zn or Pb atom, $A$ = N or P atom). **c** Bidentate structure of metal diethoxyphosphinecarbodithioic acid complex model ($M$ = Cu, Zn or Pb atom)

**Table 3.** BSSE-corrected interaction energies (kJ/mol) between different collector anions and metal cations. Geometry optimizations calculated with the HF/Huz/3-21G* level of theory using Huzinaga basis set for metal cations. The interaction energies of chelates were calculated with B3PW91/Huz/6-31G*

| Metal/ collector | Cu(I) | Pb(II) | Zn(II) | Cu(II) |
|---|---|---|---|---|
| $E_2N$ | −756 | −1541 | −1765 | −1875 |
| ENH | −751 | −1519 | −1744 | −1845 |
| $E_2P$ | −704 | −1461 | −1696 | −1785 |
| EO | −721 | −1463 | −1685 | −1785 |
| $ECH_2$ | −719 | −1444 | −1682 | −1777 |
| $(EO)_2P$ | −691 | −1435 | −1680 | −1767 |
| ES | −699 | −1443 | −1670 | −1763 |

xanthates or dialkyldithiocarbamates [23]. Table 3 also shows that the calculated interaction energies are the smallest for the ES–metal and $(EO)_2P$–metal complexes. The energy difference between these collectors and $E_2N$ is about 60–120 kJ/mol, which can be considered significant and therefore gives information on the energetically favoured structures. According to Klimpel [6], trithiocarbonates are somewhat stronger collectors than xanthates. In contrast to this, our calculations show that the interaction energies of the EO–metal complexes are slightly larger than those of the ES–metal complexes; however, the difference is at most about 20 kJ/mol, which does not allow any definite conclusions to be drawn.

## *3.3 Charges*

In addition to the interaction energies we also studied the charge distribution in the hope of discovering the reason for the effectiveness of the dithiocarbamate collectors. The charges of the metal complexes were computed by both Mulliken analysis [24] and the natural population analysis (NPA) method [25].

Figure 3 shows the charges of the groups or atoms attached directly to the $CS_2^-$ group as calculated by the NPA method. Mulliken analysis showed the same trend in the charges of these atoms and groups. The most negative charge is for the oxygen atom in xanthate (EO). The groups in ascending order from the most negative charge are $O < N < NH < CH_2 < S < P$. This order corresponds approximately to the electropositivities of the atoms and atom groups. The highest positive charge is for the $(EO)_2P$ complex, possibly because of the electron-withdrawing oxygen atoms attached to phosphorus. The charges of the carbon atoms in the thiol group are affected in the reverse order. The most electronegative oxygen atom in the xanthate collector attracts electrons most efficiently; thus, in the xanthate complexes the carbon atom has the most positive charge. In the $(EO)_2P$–metal complexes the carbon atom has the most negative charge. The charge order of the carbon atom in different complexes is opposite to that seen in Fig. 3, i.e. $(EO)_2P < E_2P < ES < ECH_2 < ENH < E_2N < EO$.

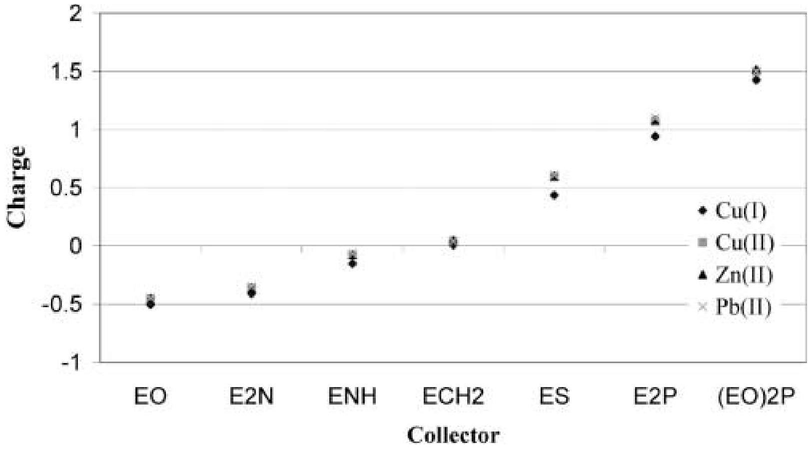

**Fig. 3.** Charges of groups or atoms directly attached to the $CS_2^-$ group calculated by the natural population analysis (*NPA*) method

The influence of neighbouring atoms and groups on the charges of the sulphur atoms in the thiol group is shown in Fig. 4. Evidently an inductive effect affects the charges. The most electropositive atoms, sulphur and phosphorus, induce a negative charge on the carbon atom, so the charge of the sulphur atoms is smaller than in the carbamate or xanthate complexes. Furthermore, in the xanthate complexes the oxygen atom is already so electronegative that it attracts electrons from the carbon and sulphur atoms. In carbamates, the nitrogen atom and the NH group lead to more evenly distributed charges between the nitrogen and the carbon atoms. There is a small negative charge on the carbon atom, and the sulphur atoms have the most negative charges of all the complexes. These highly negative charges may influence favourably the interaction energies.

Figure 4 also reveals the variation in the charge on sulphur according to the metal. The sulphur charges are most negative in Cu(I) complexes and are more positive for metals with oxidation state +II. This might be due to the different polarizing capability of the metal ions. For example, owing to their less filled *d* orbitals ($d^9$) Cu(II) ions attract electrons from sulphur atoms more effectively than do Cu(I) ions ($d^{10}$).

### *3.4 Changes in the bond lengths in complex formation*

It is assumed that the C—O bond becomes shorter when the xanthate collector forms complexes with metals. Both theoretical [26] and experimental studies [27] have been carried out on the C—O IR stretching frequencies, which seem to shift to higher frequency upon complexation. In solid potassium ethyl xanthate, the peaks at 1,100 and 1,138 $cm^{-1}$ have been assigned to asymmetric C—O—C vibration and symmetric C—O—C vibration, respectively. In addition, there are weak peaks at 1171 and 1175 $cm^{-1}$ in solid and 0.1 M aqueous potassium ethyl xanthate, respectively. The asymmetric C—O—C vibration wave numbers of the xanthate ligand are shifted upwards in the copper, iron and zinc xanthate complexes [27]. For example, the C—O vibration frequency is at 1195 $cm^{-1}$ in zinc ethyl xanthate and at 1207 $cm^{-1}$ in lead ethyl xanthate [28].

According to our calculations the bond distances between the O, N, C, S and P atoms (Fig. 2) and the carbon atom in the $CS_2M$ moiety decreased (1.4–7.5%) in all but one collector when the complex was formed. In the diethoxyphosphinecarbodithioic acid complexes [$(EO)_2P$–] the distance increased slightly (at most 2.2%) possibly owing to the electronegative oxygen atoms, which are attached directly to phosphorus. This causes the electrons to flow towards the oxygen atoms and destabilizes the complex structure. The electron-withdrawing effect of the oxygen atoms also influences the interaction energies, as seen in Table 3, where diethoxyphosphinecarbodithioic acid complexes are shown to have the weakest interaction energies.

The bond lengths between metal and sulphur atoms in the different complexes were the shortest in the diethyl dithiocarbamate complexes ($E_2N$–) and the ethyl dithiocarbamate complexes (ENH–). The short bond length in the $E_2N$ chelates can be attributed to the stabilizing effect of the nitrogen atom, as noted in Sect. 3.3. The metal–sulphur bonds were the longest for the $(EO)_2P$ chelates (0.04–0.06 Å longer than in the $E_2N$ complex). Evidently the oxygen atoms bonded to phosphorus cause bond lengthening as well as a weaker interaction energy (Table 3), because the bonds between the metal and sulphur atoms in the $E_2P$ complexes, which do not have electronegative oxygen atoms, are shorter than in the $(EO)_2P$ complexes.

## 4 Conclusions

Our study on the interactions in chelate structures between different thiol collectors and $Cu^+$, $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ cations shows that the bonds between the sulphur atoms and metal ions are strongest for dithiocarbamate anions. There is experimental evidence that dithiocarbamate ions are powerful collectors [21, 23]. The calculations establish that the strength of the interaction depends mostly on the electronic nature of the group directly attached to the thiol group. On a larger surface, however, the adsorption will not necessarily be bidentate because of the structure of the sulphide mineral. Different binding modes will certainly be possible, depending on the nature of the surface sites.

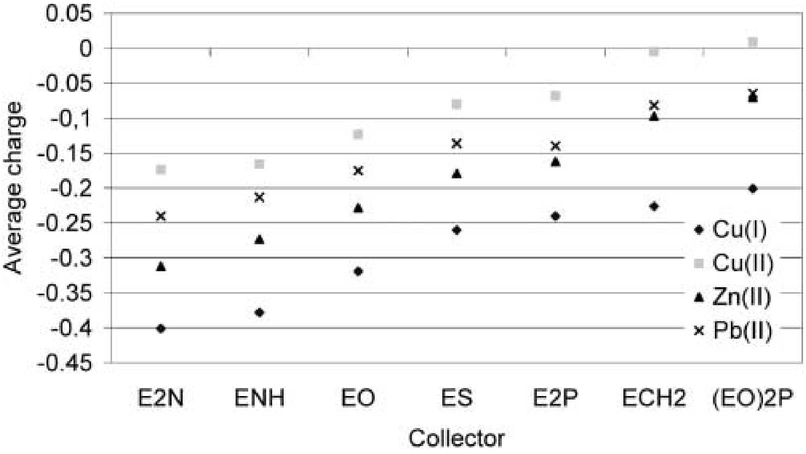

**Fig. 4.** Average charge of the two sulphur atoms in the $CS_2^-$ group calculated by the NPA method

Our single metal cation models do not represent the long-range electrostatic effect of a larger surface and a more detailed study on expanded surface models will be necessary if the topology of the real mineral surfaces is to be taken into account. The preliminary results from this work can nevertheless be used to compare the effects of the collector structure on the direct interactions of different metal ions.

In this survey we studied the interaction of the collector molecules in the gas phase. Work in the gas phase suffers from the lack of solvent effects. Since froth flotation takes place in water, we can reasonably assume that the solvent can influence the interaction energies. The solvent effects need to be taken into account, especially in modelling the interaction energies, to get quantitative information and in attempts to clarify more accurately the energy differences between the collector and the metal cation. On the other hand, since the flotation process includes several phases and the overall effect of the collectors is to make the surface hydrophobic, gas-phase calculations can also give reliable information on the relative differences in the interactions with the various collectors. Furthermore, the results can be used in a qualitative analysis of the fundamental properties of the interaction and should be helpful in the design of new and more powerful collector molecules.

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