Adsorption of Thiol Collectors on Chalcopyrite

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Abstract—Adsorption of diethyldithiocarbamate and ethylxanthate on chalcopyrite mineral surface was studied by static bed adsorption method. The qualitative nature of surface species was examined by selective solvent extraction and UV-visible spectroscopic technique. The results clearly indicate that the interaction between surface metal ions and thiols is chemical in nature. As a result of chemical interaction of ligand molecules, metal ions from mineral surface are dislodged from the lattice and precipitates of metal-ligand complexes were formed on the surface, Surface complexes were found to be identical to that of bulk complexes with metal-to-ligand ratio of 1:2.

Keywords: *Adsorption, Static bed, Chalcopyrite, Diethyldithiocarbamate, Ethylxanthate.*

INTRODUCTION

The application of xanthates and related thiol compounds like dithiocarbamates, dithiophosphates, dialkylthionocarbamates and mercaptobenzothiozoles as collectors in floatation practice is widely known since 1925. As the 3p electrons of sulphur atoms of thiols and the nd electrons of metal atoms of mineral are approximately located in the same energy level, orbitals are adequately overlapped by a nearly equal energy and similar symmetry. Consequently, a strong chemical bond is expected between thiol reagents and sulphide minerals [1]. In the case of collector molecules with oxygen as ligand atom, fixation of reagents on mineral surface is however less stable. This was attributed to the fact that the energy of donor orbitals is higher than that of hybridized molecular orbitals of sulphides. Thus, the thiol collectors are supposed to be more suitable compared to other types of collectors. Among these thiols, dithiocarbamates are particularly selective and exhibit several advantages as collectors towards copper minerals. The mesomeric electron releasing tendency of the R_2N-group of carbamates enhances the electron donating ability to metal Lewis acid sites at the mineral surface.

The adsorption of collectors on the mineral surface receives enormous attention in floatation research. The fixation of collector molecule on the mineral surface is an essential criteria to convert particle surface from hydrophilic to hydrophobic surface

so that the particle will float by adhering to an air bubble. Of all the thiol compounds, xanthates have been most extensively investigated. Different techniques like cyclic voltammetry, ellipsometry, FT-IR and X-ray photoelectron spectroscopy were tried. Several possible mechanisms such as chemisorption, ion exchange and neutral molecule adsorption were suggested by different authors [2–4]. Most of the investigations were conducted on galena-xanthate system. However, detailed investigations on the chemistry of xanthates and dithiocarbamates and their interaction with other sulphide minerals appears to be very limited. Hence, the present investigation was aimed to have better understanding of the adsorption of xanthates and dithiocarbamates on chalcopyrite, which is a chief mineral of copper. Adsorption experiments were conducted by static bed method and the surface products were characterized by spectroscopic technique. Since the thiols, especially xanthates, are sensitive to oxidation, care was taken to minimize such effects.

EXPERIMENTAL

Material: The chalcopyrite ($CuFeS_2$) sample used in the present investigation was obtained from the Chitradurga Copper Company, Karnataka, India. Pure lumps of $CuFeS_2$ were hand-picked from the above mines. The chemical analyses of the sample revealed 30.2% of Cu, 31.0% of Fe, 33.8% of S and the rest as SiO_2. The sample was ground in a pebble mill under nitrogen atmosphere to avoid surface oxidation. The specific surface area of the sample was measured by BET method and was found to be 0.73 m^2/g.

.   Potassium ethyl xanthate (EX) and sodium diethyl dithiocarbamate (DTC) were prepared and purified in the laboratory according to the established procedures suggested by Rao [5] and Thorn and Ludwig [6] respectively. The crystals of pure ethyl xanthate and dithiocarbamate were dried over silica gel and stored in a vacuum dessicator. Freshly prepared solutions were used each time. All other chemicals used were of analar grade except organic solvents like CCl_4, $CHCl_3$ and CS_2 which were of spectroscopic grade.

Methods: The adsorption experiments were conducted in a column apparatus shown in Fig. 1. An accurately weighed sample (0.1 g) was taken in a sintered glass frit and the reagent solution with known concentration and pH was passed through the mineral bed at a constant flow rate of 0.166 ml/s. All the reagent solutions were prepared in double distilled water. Nitrogen gas was bubbled through the reagent solution in order to avoid oxidation. The filtrate solutions collected at different time intervals were immediately analysed by UV-visible spectrophotometer to determine the quantity of unadsorbed reagent. Diethyldithiocarbamate was analysed at an absorption maxima of 282 nm, whereas ethyl xanthate was analysed at 301 nm, as suggested by earlier workers [5 & 6].

The surface species were characterized by extracting into a suitable organic solvent and by recording their spectra. After adsorption and before extracting with organic solvent, the mineral sample was dried under vacuum. In order to obtain a quantitative estimate of the metal ions present in the complex, metal ions were
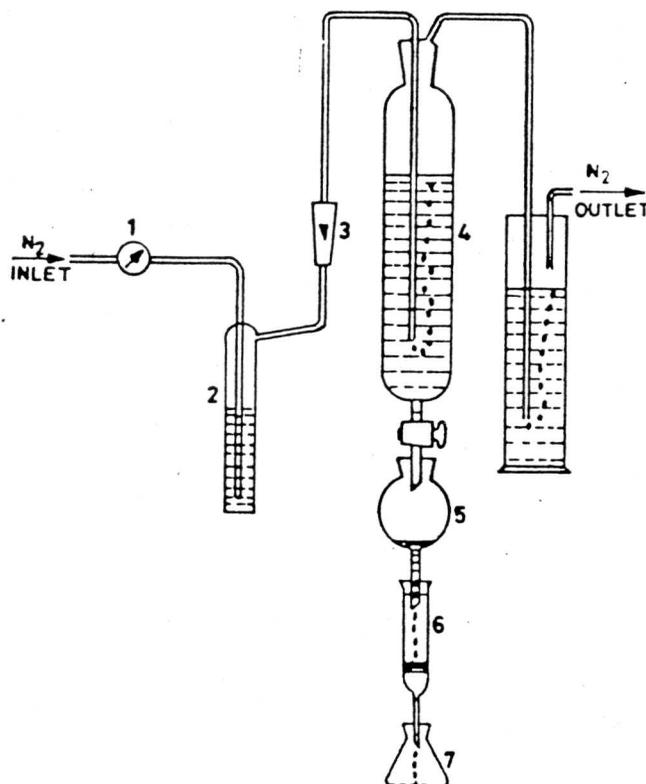
Fig. 1. Experimental set-up of static bed adsorption. 1. Pressure gauge. 2. Pyrogallol solution. 3. Rotameter. 4. Reservoir for feed solution. 5. Reagent feeder. 6. Sintered glass tube. 7. Effluent xanthate solution

stripped from an organic phase by using dil. HNO_3. The aqueous phase of the same was analysed by atomic absorption spectrophotometer.

Zeta potential measurements were conducted to find out the surface charge of the mineral. Laser Zee Meter 501 equipped with a video system was used for the purpose. All tests were conducted at a constant ionic strength of 0.1 M $NaClO_4$.

RESULTS AND DISCUSSION

CuFeS$_2$-DTC system

The adsorption of DTC on chalcopyrite at different pH conditions was studied and the results of the same present in Fig. 2. Adsorption experiments were studied in the pH region of 7.00 and 10.00 because (i) DTC is expected to undergo decomposition both in acidic and highly basic regions; and (ii) most of the sulphide minerals are floated within this pH region.

CONC.OF DTC: 11.095 x 10 mol/l
pH OF THE SOLUTION (DTC)

- ● 7.0
- △ 8.0
- ○ 9.0
- □ 10.0
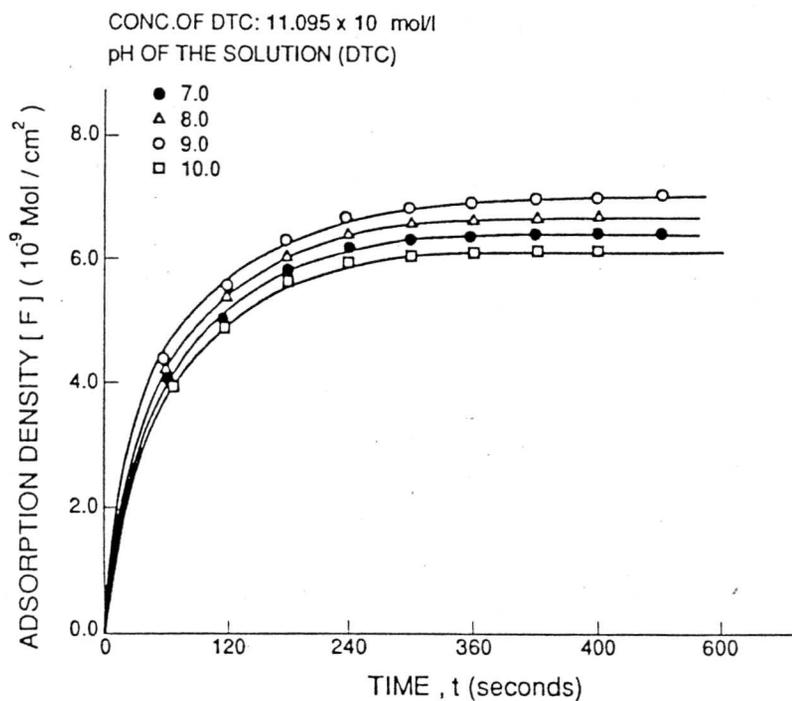
Fig. 2. Adsorption of DTC on chalcopyrite at different pH values (times versus adsorption density curves)

In the present study, though the difference in adsorption density at various pH values is very small, the maximum adsorption density was noticed around pH 9.00. It could be explained in terms of dissociation constant of DTC molecule with respect to pH. Soni and Trivedi [7] have suggested the following forms in which dithiocarbamic acid could exist:

$$
\underset{C_2H_5}{\overset{C_2H_5}{\diagdown}}N-C\overset{S}{\underset{S}{\diagup}}\underset{pK_1}{\overset{H^+}{\rightleftharpoons}}\underset{C_2H_5}{\overset{C_2H_5}{\diagdown}}N-C\overset{S}{\underset{SH}{\diagup}}\underset{pK_1}{\overset{H^+}{\rightleftharpoons}}\underset{C_2H_5}{\overset{C_2H_5}{\diagdown}}\overset{+}{N}-C\overset{S}{\underset{SH}{\diagup}} \tag{1}
$$
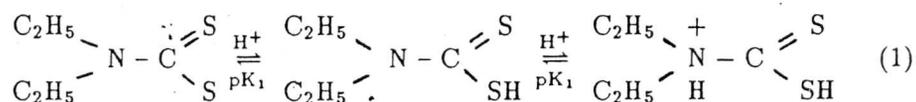
According to this proposal, dithiocarbamate is a diacidic base and exhibits two pK_a values. By analogy with tertiary aliphatic amines, $-^+NH(C_2H_5)_2$ may be considered as a weaker acidic group ($pK_a = 8.4$) and $-SH$ the stronger one ($pK_a = 7.5$). The behaviour of acidic species may be compared with that of ampholytes. The conjugate acid of the basic group $[-N(C_2H_5)_2]$ will be $[-^+NH(C_2H_5)_2]$. By taking the above pK_a values, the distribtuion diagram of three different species of

Tc/mM for DTC⁻ = 0.100
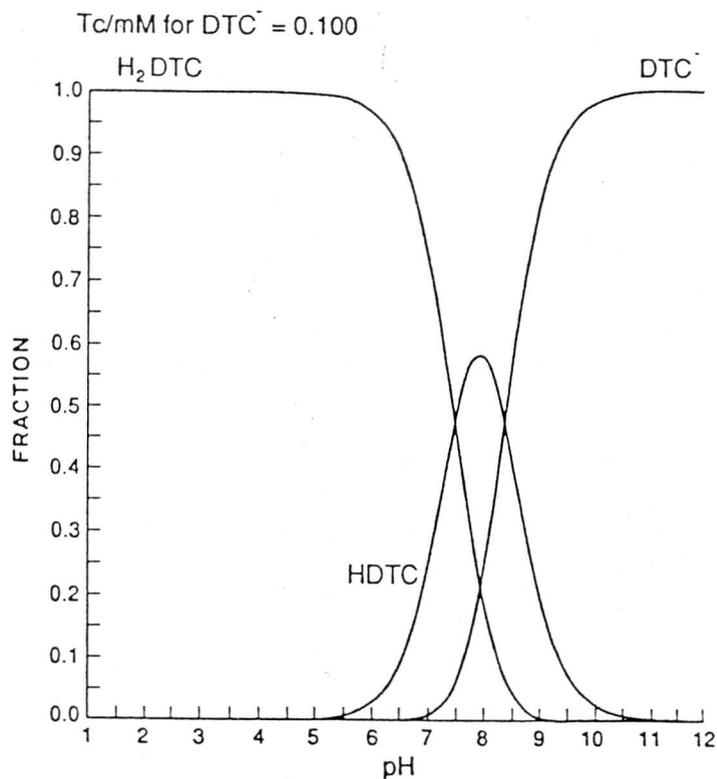
Fig. 3. Species distribuiton diagram of diethyldithiocarbamate

dithiocarbamate was constructed by the SOLGASWATER computer program [8]. The distibution diagram of the same is shown in Fig. 3. It is clear that at around pH 9.00, (DTC)⁻ is predominant. The maximum adsorption at pH 9.00 could be attributed to the effective adsorption of (DTC)⁻ compared to the other two forms of DTC. Generally, protons bonded to sulphur and nitrogen should essentially dissociate to facilitate bonding with metal ions. Thus the maximum adsorption at pH 9.00 could be explained in terms of acid dissociation constants of the dithiocarbamate molecule. It is known that dithiocarbamates are capable of forming metal complexes even in the acidic pH region, implying the complexing ability of DTC in its protonated forms. The protonated forms could probably interact with metal ions by simultaneous deprotonation mechanism, as metal complexes are more stable and favourable thermodynamically.

The characteristics of the mineral surface were also analysed by zeta potential measurements. Zeta potential of chalcopyrite in the presence and absence of DTC are shown in Fig. 4. It may be noted that the particles of $CuFeS_2$ are negatively

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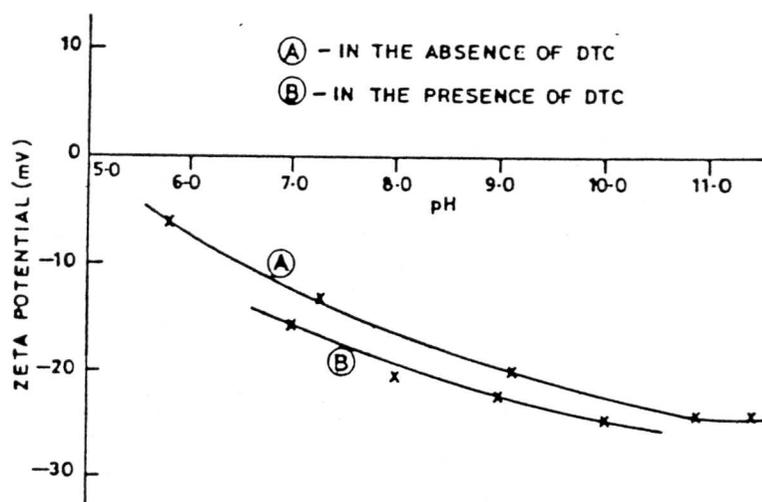
Fig. 4. Zeta-potential of chalcopyrite in the presence and absence of DTC

charged throughout the pH region studied. Since the hydroxides of both copper and iron are expected to form around pH 3.5 onwards, the surface sites of Cu and Fe at the chalcopyrite-H_2O interface will be hydroxylated around this pH. The negative charge on $CuFeS_2$ surface could be attributed to hydroxylation. Thus at pH 7.0 and above where the adsorption tests were conducted, both mineral surface and ligand molecules are negatively charged. Under these circumstances, adsorption of DTC on chalcopyrite surface by electrostatic attraction can be ruled out due to high repulsive forces operating between the two. Hence, the alternative adsorption mechanism could be apparently due to chemical interaction. The adsorption density was found to decrease beyond pH 9.0. This could be explained by the Barsky relationship [9] which will be represented as $(X^-)/(OH^-) = K$ where X^- is a ligand molecule and K is a constant. If the concentration of OH^- ions exceeds a certain limit, the adsorption of ligand molecules is inhibited due to competition between OH^- ions and DTC^- molecules. Consequently, the adsorption density will be decreased. Thus the pH of the medium plays an important role in controlling the adsorption of reagent molecules at mineral-solution interface.

A set of experiments were conducted at various concentrations of DTC and at constant pH of 9.0. The results of this are shown in Fig. 5. the adsorption density plotted against time indicate a hyperbolic relationship. As the concentration of DTC increases, the adsorption density was found to increase gradually. The sharp increase in adsorption density during the initial stages within a short time also suggests a chemical interaction between DTC and $CuFeS_2$. If the adsorption process was a true chemisorption of Langmuir type, it would have been restricted to a monolayer. By taking the cross-sectional area of DTC as 37 $Å^2$ [6], complete monolayer forma-

pH OF DTC SOLUTION: 9.00

CONCENTRATION OF D.T.C. x 10^4 mol / l

$\circ$ 4.4381
$\triangle$ 6.6571
$\square$ 8.8762
$\bullet$ 11.095
$\star$ 13.314
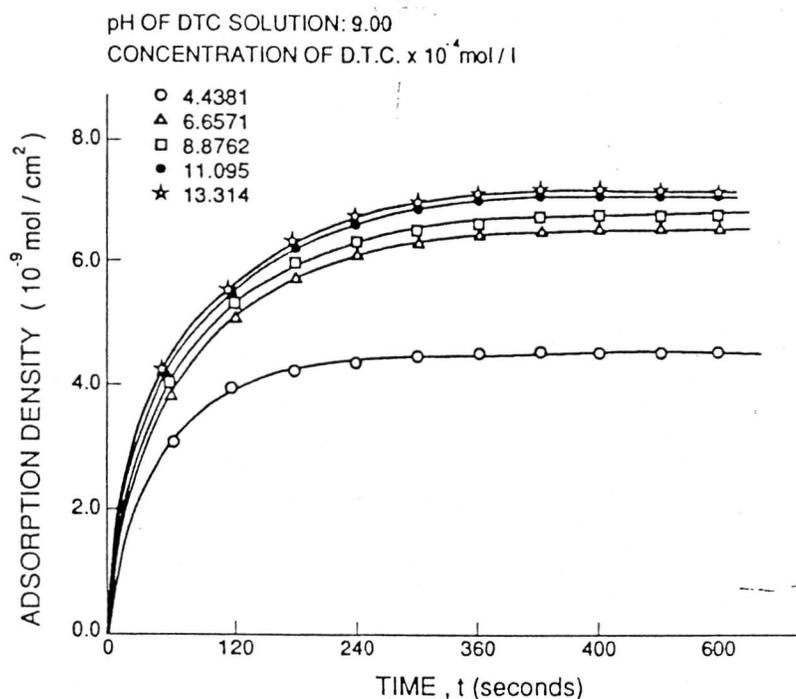
Fig. 5. Effect of DTC concentration on adsorption density

tion is expected around the adsorption density of 4.5×10^{-10} mol/cm^2. However, adsorption density at plateau value corresponds to 10–16 layers, depending on the concentration of DTC. In the Langmuir model, the adsorbed molecules are allowed to interact with the adsorbent but not with each other. Once the surface is fully covered with DTC molecules, it should not have further influence on the system. From the experimental facts, it is clear that the adsorption process is governed neither by electrostatic nor by true chemisorption. In order to have better understanding, surface products were extracted with a suitable solvent and analysed by UV-visible spectroscopic methods.

After the adsorption, the mineral was transferred into a beaker and treated with CCl$_4$ (which is an exceellent solvent for metal-dithiocarbamate complexes). The CCl$_4$ extract thus obtained was subjected to UV-visible spectroscopic technique. The spectrum recorded (Fig. 6) was found to be similar to that of Cu(DTC)$_2$ complex in bulk solution. The broad peak observed at 435 nm is the characteristic peak of Cu(DTC)$_2$ and is attributed to the large charge transfer between metal ion and ligand (M $\Leftrightarrow$ L). The other two peaks around 255 and 260 nm with relatively sharp and high absorbance are attributed to intraligand transitions such as n $\rightarrow$ σ^*, n $\rightarrow$ Π^* and Π $\rightarrow$ Π^* [10]. The possibility of formation of complexes like Cu(I) DTC
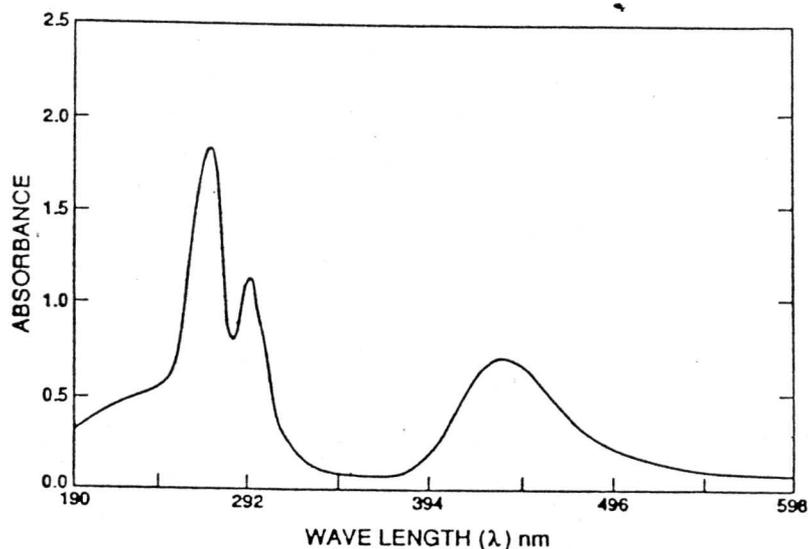
Fig. 6. UV-visible spectrum of surface product (extracted into CCl₄ after adsorption of DTC on chalcopyrite)

and [Cu DTC]⁺ were also explored. Metal ligand transitions in Cu(I) DTC and [Cu DTC]⁺ are expected to appear at a lower wavelength of 385 nm [11]. Since there is no peak at 385 nm, it may be assumed that such complexes are absent in the system. The peak regarding iron diethyl dithiocarbamate was found to be absent in the spectrum of surface products. Usually, $Fe(DTC)_3$ exhibits a broad peak around 515 nm in CCl_4. The absence of iron in the extract of surface product was further confirmed by AAS.

After thorough extraction of the surface product into CCl_4, metal ions of the complex were stripped into an aqueous solution by treating with dilute HNO_3. The concentration of metal ions was estimated by atomic absorption spectrophotometer. Interestingly, the quantity of iron present in the complex was found to be neglibible. The complexation of DTC with Cu and Fe can be represented as

$$Cu^{2+} + DTC^- \rightleftharpoons [Cu \ DTC]^+ \qquad \log K = 12.5 \qquad (2)$$

$$Cu^{2+} + 2DTC^- \rightleftharpoons Cu \ (DTC)_2 \qquad \log K = 24.0 \qquad (3)$$

$$Fe^{3+} + 3DTC^- \rightleftharpoons Fe \ (DTC)_3 \qquad \log K = 11.34 \qquad (4)$$

The large gap between the formation constants of $Cu(DTC)_2$, and $Fe(DTC)_3$ clearly explains the selectivity of DTC towards copper. Thus, the copper minerals can be selectively separated from gangue minerals like pyrite and pyrrhotite (iron

sulphides) by using DTC as collector. The stoichiometry between absorbed DTC molecules and the number of copper atoms, estimated from the surface product, was found to match with $Cu(DTC)_2$ complex. In other words, the ratio of Cu to DTC was found to be 1 : 2. Furthermore, the total copper atoms in the surface product was found to be more than the surface atoms calculated theoretically from the crystal structure data. This shows that the subsequent layers of copper atoms placed below the outermost plane were also reacted with DTC. Due to strong complexation between DTC and surface copper atom, cleavage of bonds between surface copper atom and other lattice atoms is expected. Since DTC is a bidentate molecule, each DTC can occupy two coordination sites. Due to the newly-formed coordination bond between DTC and surface copper ion and subsequent fracture of bonds with lattice atoms, surface copper atoms were dislodged from the surface lattice sites. Newly-formed $[Cu\, DTC]^+$ species in turn react with one more DTC molecule to form a stable $Cu(DTC)_2$ complex. Thus, the interaction between DTC molecule and surface copper sites leads to the formation of $Cu(DTC)_2$ complex with a square planar structure.

From the aboive discussion, it is apparent that the adsorption process between mineral surface and dithiocarbamate is mainly governed by a chemical reaction. The interaction between particle surface and DTC is, therefore, expected to proceed through the following steps.

(a) Diffusion of ligand molecules to the interface;

(b) Adsorption at the interface;

(c) Reaction at the interface; and

(d) Desorption of products.

As a result of diffusion, adsorption and reaction of DTC with the mineral surface, a stagnant film (boundary layer) of the metal-DTC complex is formed around each particle. Consequently, diffusion of ligand molecules will be prevented.

The pH of the reagent solution was measured after passing through the mineral bed. The pH was found to shift towards a more basic range after adsorption. This could be explained due to chemisorption of water molecule [12] prior to the adsorption of DTC. Because of the faster diffusion of water molecules compared to bulky ligand molecules, the mineral surface is hydrated at the initial stage as represented:

$$\equiv Cu \atop \equiv S \quad + H_2O \rightleftharpoons \quad \equiv Cu - OH \atop \equiv SH \tag{5}$$
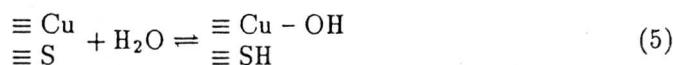
In the second stage, the $[DTC]^-$ ions may interact with metal ions by repalcing OH^- ion via ion exchange mechanism.

$$\equiv Cu - OH \atop \equiv SH \quad {[DTC]^- \atop \rightleftharpoons} \quad \equiv \atop \equiv SH \ + [CuDTC]^+ + OH^- \tag{6}$$
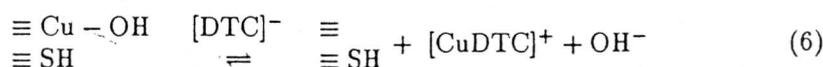
The increase in pH could be attributed to the above ion exchange mechanism. Since $[CuDTC]^+$ is highly unstable, it, in turn, reacts with the second $[DTC]^-$ molecule as represented below.

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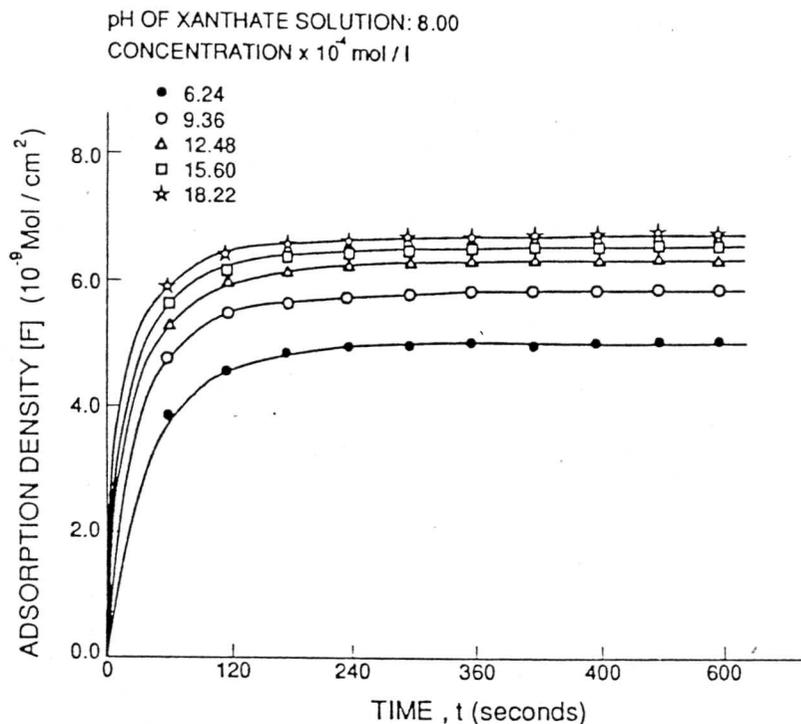
Fig. 7. Effect of xanthate concentration on adsorption density

$$[CuDTC]^+ + [DTC]^- \rightleftharpoons Cu(DTC)_2 \qquad (7)$$
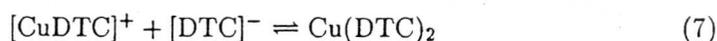
Thus, the precipitate of $Cu(DTC)_2$ is formed on the mineral surface.

Chalcopyrite-Xanthate System

The kinetics of xanthate adsorption on $CuFeS_2$ was followed at various concentrations and the results of the same plotted in Fig. 7. As the concentration increases, the adsorption density was found to increase as observed in the case of DTC. Considering the cross-sectional area of xanthate molecule as 29 Å^2[13], the adsorption density of the plateau value was observed to be several times more than the monolayer. In-order to verify the nature of surface product, the surface product was extracted into chloroform and the UV-visible spectrum was recorded. This spectrum, shown in Fig. 8, resembles that of cupric xanthate [14]. The broad peak observed around 415 nm is a characteristic peak of $Cu(EX)_2$. The composition of metal ions in the organic phase was also analysed by AAS after stripping the same into an aqueous phase. The mole ratio of copper to xanthate is very close to 1 : 2. This clearly illustrates the formation of Cu(II) xanthate on the surface of chalcopyrite.
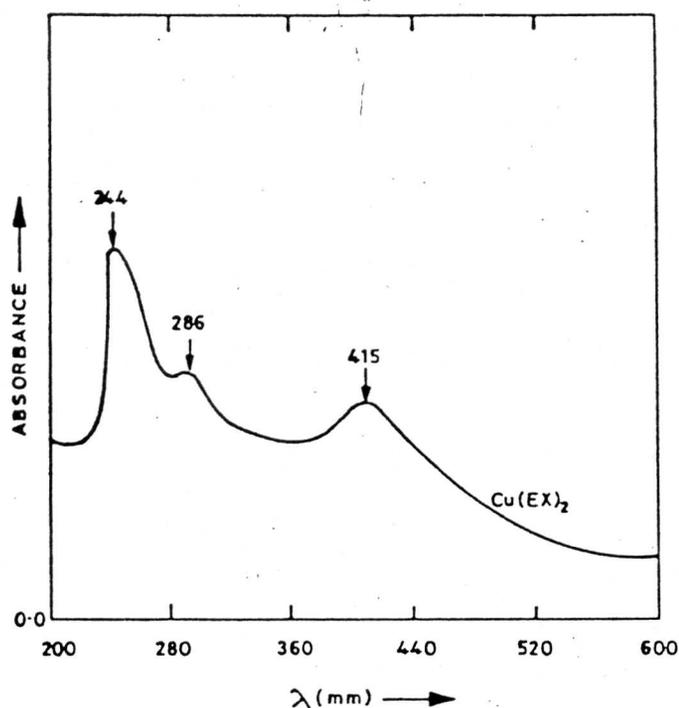
Fig. 8. UV-visible spectrum of surface product (extracted into CHCl₃ after adsorption of xanthate on chalcopyrite)

According to Taggart [15] and Sutherland and Wark [16], the formation of Cu(II) xanthate was very unstable and exists only transitionarily. The Cu(II) xanthate will be converted to Cu(I) xanthate and dixanthogen as represented below.

$$2Cu(EX)_2 \ \rightleftharpoons \ 2Cu(EX)^+ + Dx(Dixanthate) \tag{8}$$
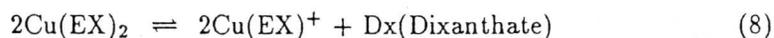
It may be noted that the rate of dixanthogen formation is high in the presence of oxygen and also in the presence of a solvent in which dixanthogen is highly soluble. Since the experiments were conducted in the absence of oxygen and in aqueous media where the solubility of dixanthogen is negligible, the forward reaction is retarded/restricted. Consequently, the reduction of Cu(II) to Cu(I) is depressed. Hence, $Cu(EX)_2$ will remain as a main product on the mineral surface. Tests conducted to identify the presence of dixanthogen were found to be negative. Yamasaki and Nanjo [17] have confirmed the formation of $Cu(EX)_2$ by using ESR technique. They concluded that the precipitate formed by the reaction between Cu^{2+} ion and ethyl xanthate in aqueous media is invariably a $Cu(II)(EX)_2$ and it only dissolves by forming complex $(CuEX)^+$ in the presence of excess Cu^{2+} ions.

$$Cu(EX)_2 + Cu^{2+} \rightleftharpoons 2(Cu\ EX)^+ + 2EX^- \tag{9}$$
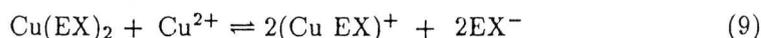
Leja [18] has observed the formation of cationic copper xanthate complex $[CuEX]^+$ similar to the mechanism suggested above. Such type of positively-charged complex, initially formed on the surface, in turn adsorb on negatively-charged $CuFeS_2$ by electrostatic interaction. The same may be converted to $Cu(EX)_2$ by further addition of xanthate. Thus, it can be concluded that $Cu(EX)_2$ is the main species formed on the mineral surface.

Various investigators [19] have suggested three different mechanistic routes of adsorption where a chemical bond is involved: (i) *Chemisorption:* Interaction of the ligand with the surface without movement of metal atoms from their lattice sites. In such cases, adsorption is limited to a monolayer. (ii) *Surface reaction:* Interaction of the ligand molecules with the surface together with the movement of metal atoms from their lattice sites. Multi-layers of reaction product are formed in such a case. (iii) *Bulk precipitation:* Interaction of ligand molecule and metal ions away from the surface into the bulk solution. If the rate of metal dissolution and diffusion through the boundary layer is faster than diffusion of ligand molecule to the surface, bulk precipitation may occur. However, this type is mainly restricted to bulk reactions. Hydroxylation of cations on the mineral surface may assist surface reaction phenomena by providing some initial surface atom movement. From the present investigation, it is apparent that the adsorption process between mineral surface and thiol reagents is governed by chemical reaction.

CONCLUSION

The adsorption behaviour of thiol collectors, viz. diethyldithiocarbamate and ethyl xanthate on chalcopyrite was studied by static bed adsorption method and UV-visible spectroscopic techniques. Both the reagents were found to interact specifically with copper sites of $CuFeS_2$ and form respective cupric complexes with a copper-to-ligand ratio of 1 : 2. It was observed that more than a layer of surface copper sites were reacted, indicating a chemical reaction between $CuFeS_2$ and thiol ligands.

ACKNOWLEDGEMENTS

REFERENCES

1. O.S. Bogdanov, A.K. Podnek, V.I. Rjaboy and N.A. Janis. Proc of the XII IMPC, Sao Paulo, Brazil, 28 Aug.–3 September 1977, Vol. II, p. 280.
2. J. Leja, L.H. Little and G.W. Poling *Trans. IMM,* 72, 414 (1963).
3. R. Tolun and J.A. Kitchener. *Trans. IMM*, 73, 312 (1964).
4. M.A. Cook. *Trans AIME*, 220, 444 (1961).
5. S.R. Rao. *Xanthates and Related Compounds.* Marcel Dekker, New York (1971) p. 504.

6. G.D. Thorn and R.A. Ludwig. *The Dithiocarbamates and Related Compounds.* Elsevier, Amsterdam, (1962) p. 152.

7. K.P. Soni and A.M. Trivedi. *J. Ind. Chem. Soc.,* 37, 249 (1960).

8. G.A. Eriksson. *Anal Rev.,* 65, 177 (1965).

9. G. Barsky. *Trans AIMME,* 112, 236 (1934).

10. M.L. Shankaranarayana and C.C. Patel. *Acta Chem. Scand.,* 19, 1113 (1965).

11. G. Bhaskar Raju and Willis Forsling. *Colloids and Surfaces,* 60, 53 (1991).

12. G.A. Perks. *Chem. Rev.,* 65, 177 (1965).

13. A. Granville, N.P. Finkelstein and S.A. Allison. *Trans. IMM.* Sec. C 81, 1 (1972).

14. G.H. Morrison and H. Freiser. *Solvent Extraction in Analytical Chemistry.* Wiley, New York (1957).

15. A.F. Taggart. *Handbook of Mineral Dressing.* John Wiley and Sons, Inc, New York (1947).

16. K.L. Sutherland and I.W. Wark. *Principles of Flotation.* Aust. Inst. Min. Met. Inc., Melbourne (1955) p. 93.

17. Taro Yamasaki and Michio Nanjo. The Science Reports of the Research Institutes Tohoku University, Series A 21 (1969) p. 45.

18. J. Leja. *Surface Chemistry of Froth Flotation. A Textbook.* Plenum Press, New York (1982) p. 758.

19. Pradip and D.W. Fuerstenau. *Colloids and Surfaces* 8, 103 (1983).