Adsorption mechanism of diethyldithiocarbamate on covellite, cuprite and tenorite

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Abstract

Adsorption of diethyldithiocarbamate (DTC) on covellite, cuprite and tenorite was investigated under different experimental conditions. The qualitative nature of surface species formed at the interface was examined by selective solvent extraction and UV–visible spectrophotometric techniques. The presence of surface species such as $[Cu(DTC)]^+$, $Cu(DTC)_2$ and Cu(I) DTC at different concentrations of the reagent and pH of the suspension was investigated. The results of this study indicate a surface reaction between DTC ligand molecules and surface copper sites. As a result of interaction with DTC, cations on the mineral surface are dislodged from the lattice and precipitated on the surface as copper dithiocarbamate complexes. Depending on the concentration of DTC, two types of copper complexes, i.e. $[Cu(DTC)]^+$ at low concentration and $Cu(DTC)_2$ at higher concentration, are noted on copper(II) substrates, whereas on cuprite Cu(I) DTC was formed along with $[Cu(DTC)]^+$ and $Cu(DTC)_2$. From the kinetic study, the overall adsorption was found to be mainly controlled by diffusion processes.

INTRODUCTION

The application of xanthates and related thiol compounds (dithiocarbamates, dithiophosphates, dialkylthionocarbamates and mercaptans, etc.) as collectors in sulphide mineral flotation has been widely known since 1925 [1–4]. Among these thiols, dithiocarbamates are particularly selective and exhibit several advantages as collectors for copper minerals. The mesomeric electron releasing tendency of the R_2N group enhances the electron donating ability to metal Lewis acid sites at the mineral surface. In addition, vacant d-orbitals of S atoms are capable of accepting the nd electrons from metal ions forming an additional dative π bond [5]. These two properties of dithiocarbamates are highly favourable and substantially contribute to the formation of a strong coordinate bond. Furthermore, dithiocarbamates are more hydrophobic (owing to the presence of two alkyl groups) than xanthates.

Since dithiocarbamates fulfil many of the essential requirements of collectors, several researchers have studied this class of reagents for beneficiation of various minerals [6–8]. Recent investigations on the beneficiation of mixtures of copper oxides, carbonates, sulphides and arsenopyrite have revealed that dithiocarbamates are more promising than xanthates in this regard. It has been proved that a mixture of copper minerals can be effectively beneficiated without prior sulphidisation by using dithiocarbamates as collectors [6,7]. However, very little attention has been paid to the understanding of the mechanism of dithiocarbamate adsorption on mineral substrates. The present investigation was undertaken with the aim of describing the adsorption mechanism of dithiocarbamates on copper(I) and copper(II) minerals.

Though there are reservations about the applicability of surface product analysis by extraction, in this particular case they can be ignored for the following reasons.

(1) The interaction between dithiocarbamates and surface metal ions was found to be a true chemical reaction [6].

(2) No water molecules are explicitly involved in the copper–dithiocarbamate complex.

In situ methods are essential where water molecules play a dominant role in the stability of surface species and also if the nature of reagent adsorption is physical.

The surface products formed were analysed after extracting with organic solvents and recording their UV–visible spectra under various experimental conditions.

MATERIALS

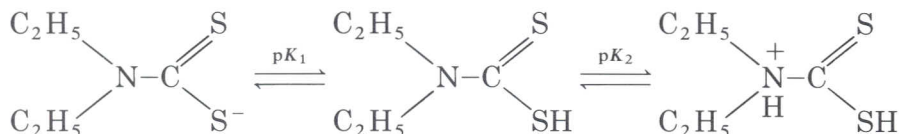Details of the synthetic covellite, cuprite and tenorite used in this work are given in Table 1.

TABLE 1
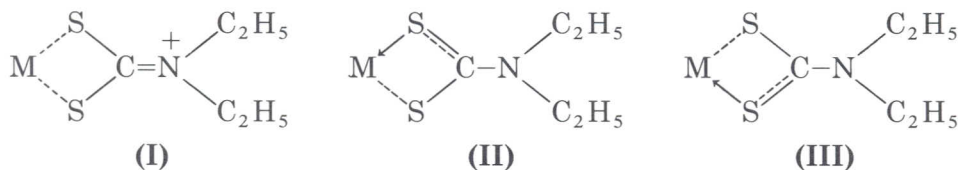
Properties of synthetic mineral samples

Material	Solubility product, K_{Sp}	Surface area $(m^2 \, g^{-1})$	Minimum assay (%)	Maximum impurities (%)		Source
Covellite (CuS)	$6 \cdot 10^{-36}$	0.60	98.5	Alkali	: 1.0	Kebo
				Fe	: 0.1	
Tenorite (CuO)	$2.2 \cdot 10^{-20}$	5.92	99.0	Alkali	: 0.2	Merck
				SO_4^{2-}	: 0.25	
Cuprite	$1.0 \cdot 10^{-14}$	2.15	94.0	CuO	: 5.0	BDH

The sodium salt of diethyldithiocarbamate (DTC) was synthesised and purified in the laboratory according to the procedure of Klopping and Van der Kerk [9]. The CCl_4 and ethanol used in this investigation were of spectroscopic grade; all other chemicals were AnalaR grade.

Soni and Trivedi [10] have suggested the following forms in which the dithiocarbamic acid may exist:

$$C_2H_5 \diagdown \underset{C_2H_5 \diagup}{N-C} \diagup\overset{S}{\diagdown S^-} \quad \underset{pK_1}{\rightleftharpoons} \quad C_2H_5 \diagdown \underset{C_2H_5 \diagup}{N-C} \diagup\overset{S}{\diagdown SH} \quad \underset{pK_2}{\rightleftharpoons} \quad C_2H_5 \diagdown \underset{C_2H_5 \diagup}{\overset{+}{N}\underset{H}{-}C} \diagup\overset{S}{\diagdown SH}$$

According to this proposal sodium diethyldithiocarbamate is a diacidic base and exhibits two pK_a values. By analogy with tertiary aliphatic amines, $-\overset{+}{N}H(C_2H_5)_2$ may be considered as the weaker acidic group ($pK_2 = 8.4$) and $-SH$ the stronger ($pK_1 = 7.5$). Dithiocarbamates form complexes with various metal ions via the sulphur atoms. Three canonical structures (I–III), may be written for the dithiocarbamate group in $M(S_2CNR_2)_n$, where M is a metal atom and n is its valency:

$$\underset{(I)}{M\diagdown\overset{S}{\underset{S}{\diagup}}C=\overset{+}{N}\diagdown\overset{C_2H_5}{\underset{C_2H_5}{\diagup}}} \qquad \underset{(II)}{M\diagdown\overset{S}{\underset{S}{\diagup}}C-N\diagdown\overset{C_2H_5}{\underset{C_2H_5}{\diagup}}} \qquad \underset{(III)}{M\diagdown\overset{S}{\underset{S}{\diagup}}C-N\diagdown\overset{C_2H_5}{\underset{C_2H_5}{\diagup}}}$$

All three forms contribute about equally to the structures of N,N-diethyldithiocarbamic acid derivatives.

METHODS

Specific surface area

The specific surface area of the samples was determined by nitrogen adsorption using the single point differential method with an Area Meter II from Strohlein.

Adsorption

50 ml of reagent solution with a known concentration of DTC and at a given pH was transferred to a flask and 1.0 g (accurately weighed)

of mineral sample was introduced. The suspension was equilibrated for 15 min under constant agitation. After attaining equilibrium, the suspension was filtered off, thoroughly washed with doubly distilled water at pH 6.8 and dried under vacuum. The filtrates were analysed for unadsorbed reagent using UV–visible spectrophotometry. The sodium salt of DTC displays two absorption peaks: one in the neighbourhood of 255 nm and the other, slightly more intense, at about 282 nm. Preliminary experiments were conducted on the decomposition of dithiocarbamate at various pH values. Spectra of DTC were found to be unaltered and stable between pH 7.0 and 12.0 for several hours, and consequently all experiments were performed within this pH range. In the case of kinetic experiments, filtrate solutions were analysed at various time intervals and the amount of unadsorbed DTC was estimated by UV–visible spectrophotometry.

Surface product analysis

Surface products were extracted from the dried samples using two different organic solvents: CCl_4 and ethanol. Ethanol was found to be a good solvent for all types of copper complexes such as $[Cu(DTC)]^+$, $Cu(DTC)_2$ and Cu(I) DTC, whereas non-ionic and less polar complexes like $Cu(DTC)_2$ and Cu(I) DTC are selectively soluble in CCl_4. A qualitative analysis of the complexes/surface products was made by UV–visible spectrophotometry. All types of pure copper complexes were prepared [11,12] and their UV–visible spectra were recorded both in ethanol and CCl_4 for comparison with the spectra of surface products.

Determination of metal ions

After extracting the surface products with CCl_4, the metal ions present in the complexes were stripped into aqueous solution and measured by atomic absorption spectrophotometry (AAS). Similarly, the very small quantity of copper–DTC complex present in the filtrate was also extracted with CCl_4. Analysis of copper in the surface products and in the filtrate provides better information for the mass balance of DTC.

Zeta potential measurements

Zeta potential measurements were conducted at a constant ionic strength of 0.1 M $NaClO_4$ using a Laser Zee Meter 501 equipped with a video system.

RESULTS AND DISCUSSION

The increase in adsorption density with time and the effect of equilibrium concentration of DTC in solution on the adsorption density are plotted in Figs 1 and 2 separately for covellite, cuprite and tenorite.
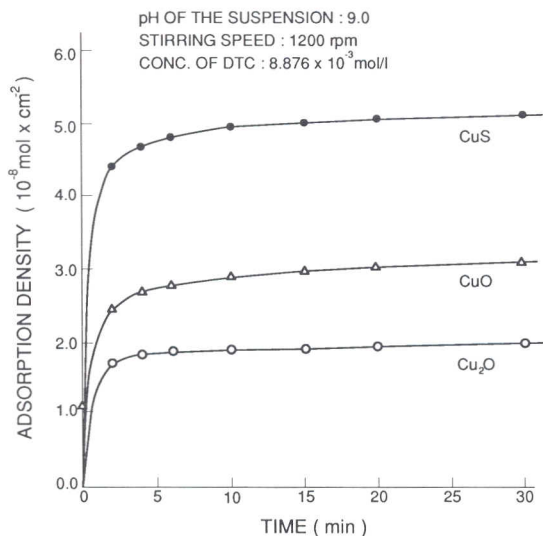

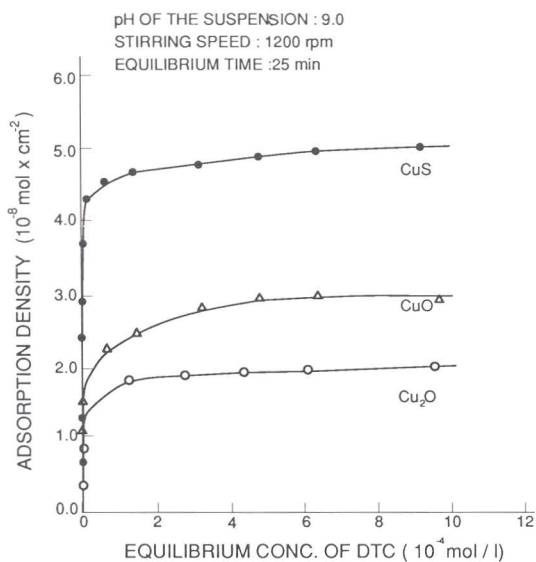Fig. 1. Time vs adsorption density curves for covellite, tenorite and cuprite.

Fig. 2. Adsorption isotherms of covellite, tenorite and cuprite.

The IR and far-IR studies conducted earlier [6] on malachite and azurite have quite conclusively established the fact that DTCs do adsorb with chemical bond formation at the mineral–water interface. Various investigators [13–15] have suggested three mechanistic routes where a chemical bond is involved.
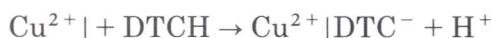
(1) Chemisorption. Interaction of the reagent with the surface without movement of metal atoms (ions) from their lattice sites. Adsorption is limited to a monolayer.

(2) Surface reaction. Interaction of the reagent with the surface together with movement of metal atoms from their lattice sites. Multilayers of reaction product may form.

(3) Bulk precipitation. Interaction of metal ions and reagent 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 collector to the surface, bulk precipitation may occur. Hydroxylation of cations in the mineral surface may assist surface reaction phenomena by providing some initial surface atom movement. Readsorption of hydrolysed species may participate in the surface reaction.

The probable chemical interactions of DTC at a mineral–water interface are summarised below. In these reactions a metal ion Cu^{2+} to the left of the vertical line designates that it is in its lattice position, while a metal ion to the right of the vertical line indicates that the ion is considered to have moved from its lattice position.
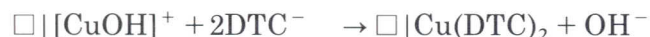
Chemisorption:

$$Cu^{2+}| + DTC^- \rightarrow Cu^{2+}|DTC^-$$
$$Cu^{2+}| + DTCH \rightarrow Cu^{2+}|DTC^- + H^+$$
$$Cu^{2+}| + OH^- \rightarrow Cu^{2+}|OH^-$$

Adsorption with surface reaction:

$$Cu^{2+}| + DTC^- \rightarrow \square|[Cu(DTC)]^+$$
$$Cu^{2+}| + DTCH \rightarrow \square|[Cu(DTC)]^+ + H^+$$
$$Cu^{2+}| + OH^- \rightarrow \square|[CuOH]^+$$

Surface reaction:

$$\square|[Cu(DTC)]^+ + DTC^- \rightarrow \square|Cu(DTC)_2$$
$$\square|[CuOH]^+ + DTC^- \rightarrow \square|[Cu(DTC)]^+ + OH^-$$
$$\square|[CuOH]^+ + DTCH \rightarrow \square|[Cu(DTC)]^+ + H_2O$$
$$\square|[CuOH]^+ + 2DTC^- \rightarrow \square|Cu(DTC)_2 + OH^-$$

If the adsorption process was a true chemisorption, adsorption would be restricted to a monolayer. When the cross-sectional area of DTC is taken as 37 Å^2, complete monolayer formation is expected at the adsorption density of $4.5 \cdot 10^{-10}$ mol cm^{-2}. From Fig. 2, the adsorption density at the plateau value corresponds to as many as 40–80 layers depending on the mineral.

The UV–visible spectra of surface products were found to be almost identical to those of copper–DTC complexes in bulk solution. Furthermore, the amount of copper in the surface product estimated by AAS after extraction with CCl$_4$ was found to be ≈ 5 times more than the surface copper atoms. From the above analysis, it is apparent that the interaction of DTC with lattice metal ions invariably proceeds via chemical reaction.

When the mineral particles are in contact with an aqueous suspension of DTC, the DTC ligands may interact either directly with metal sites or through the hydroxylated metal species at the interface. It was noticed that the pH of the suspension shifts towards alkaline during the adsorption process. Table 2 shows the initial pHs of DTC solutions and the values recorded after equilibration with covellite particles. The same trend was noted with cuprite and tenorite. This shift in pH is usually attributed to ligand exchange releasing hydroxyl ions into bulk solution. The shift in pH suggests that chemisorption of water molecules [16] occurs prior to the adsorption of DTC molecules because of the faster diffusion of H$_2$O (compared with bulky ligand molecules) to the interface:
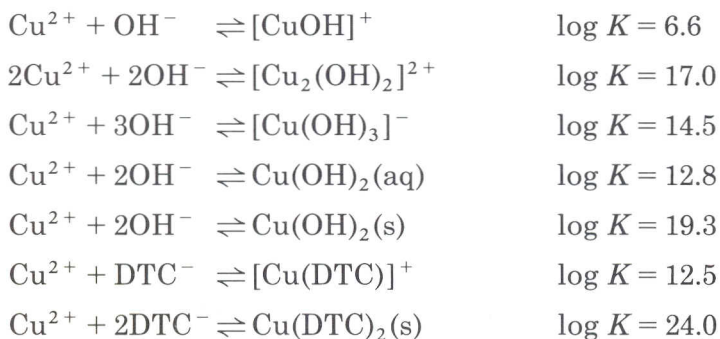
$$Cu| + H_2O \quad Cu|OH \quad \square|CuOH$$
$$S \ | \quad \xrightarrow{} \quad S \ |H \quad \xrightarrow{} \quad S \ |H$$
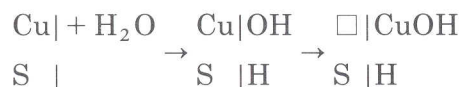
Two types of copper dithiocarbamate complexes, i.e. [Cu(DTC)]$^+$ and

TABLE 2

pH values of six DTC suspensions ($1.775 \cdot 10^{-3}$ mol l^{-1}) and corresponding values recorded after equilibration with covellite

Sample	Initial pH	Final pH
1	5.670	7.760
2	5.965	8.508
3	7.695	8.715
4	8.754	9.105
5	9.702	10.052
6	10.060	11.183

$Cu(DTC)_2$, are thermodynamically possible on copper(II) substrates depending on the concentration of DTC. The distribution of various copper species was calculated at pH 9.0 using the SOLGASWATER computer program [17] and the results obtained are incorporated in Figs 3 and 4. The following stability constants were used in the above calculation [11,18]:

$$Cu^{2+} + OH^- \rightleftharpoons [CuOH]^+ \qquad \log K = 6.6$$

$$2Cu^{2+} + 2OH^- \rightleftharpoons [Cu_2(OH)_2]^{2+} \qquad \log K = 17.0$$

$$Cu^{2+} + 3OH^- \rightleftharpoons [Cu(OH)_3]^- \qquad \log K = 14.5$$

$$Cu^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2(aq) \qquad \log K = 12.8$$

$$Cu^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2(s) \qquad \log K = 19.3$$

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

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

At a very low concentration of DTC, $[Cu(DTC)]^+$ will be the predominant species on the surface. Since the interaction of DTC with surface metal sites is of chemical reaction type, the metal ions are dislodged from the lattice along with reagent molecules and thus $[Cu(DTC)]^+$ will be precipitated on the surface. Also, DTC can interact via copper
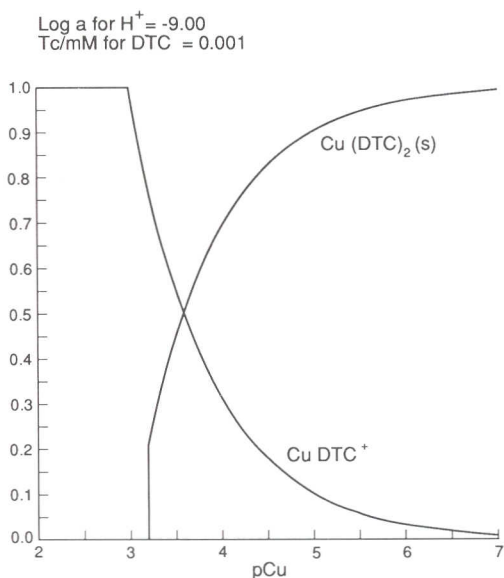
Fig. 3. Distribution diagram of Cu^{2+}–DTC^- species as a function of pCu at constant pH of 9.0.

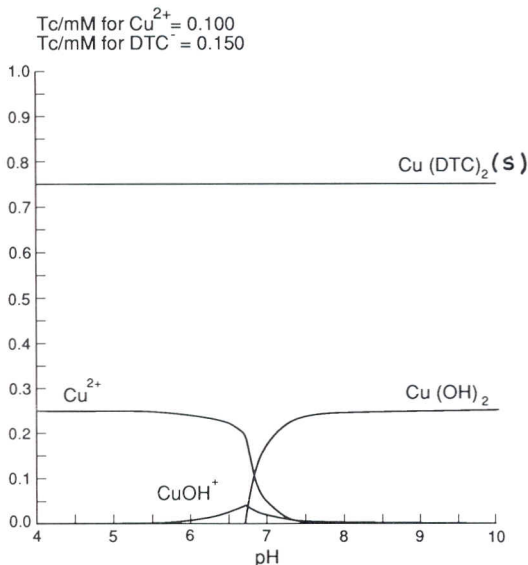Tc/mM for Cu^{2+} = 0.100
Tc/mM for DTC^- = 0.150

Fig. 4. Distribution diagram of copper species as a function of pH.

hydroxylated species precipitated on the surface as mentioned earlier. A thermodynamic basis for such surface precipitation processes has recently been proposed [19]. The $[Cu(DTC)]^+$ will be converted into $Cu(DTC)_2$ by further reaction with DTC ligands.

The formation of $[Cu(DTC)]^+$ at the interface was further confirmed by zeta potential measurements. Figure 5 shows the zeta potential behaviour of covellite, cuprite and tenorite at various adsorption densities of DTC. At very low adsorption densities, the zeta potential of covellite and tenorite particles was found to shift towards less negative values. Further increase in adsorption densities beyond $0.8 \cdot 10^{-9}$ mol cm^{-2} results in the zeta potentials dropping slowly back to negative values until they stabilize at -30 mV, the value corresponding to pure $Cu(DTC)_2$ precipitate. The extrapolated lines indicate the zeta potentials of the respective minerals in the absence of DTC at pH 9.0. Since the zeta potential measurements were conducted above the pH of the actual point of zero charge, PZC, (pH 8.01) of copper hydroxide precipitate [20], zeta potential values above this pH are ascribed to the presence of copper hydroxy species similar to that of precipitation. When DTC ligands adsorb and react on such surfaces, $[Cu(DTC)]^+$ species are formed on the surface. The initial shift of zeta potential in the positive direction supports the existence of $[Cu(DTC)]^+$ on the surface.

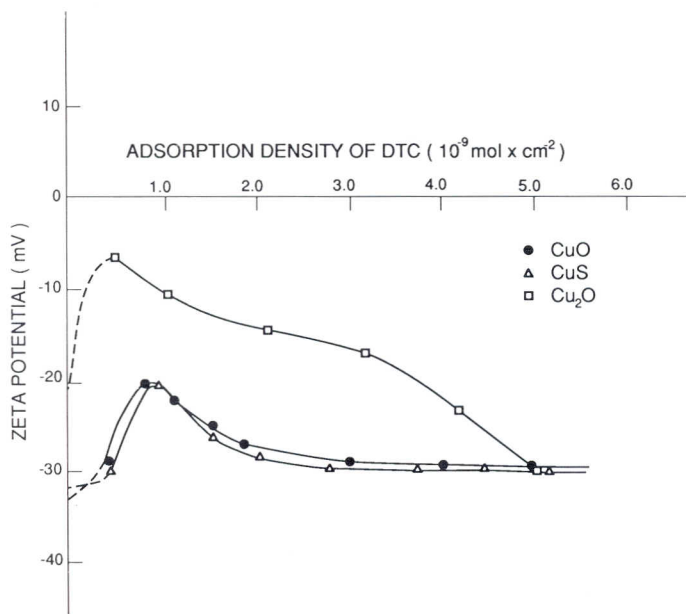Zeta potential experiments were conducted at high electrolyte con-

Fig. 5. Variation of zeta potential with adsorption density at pH 9.0.

centrations so that a shear plane can be located within the stern layer ($\zeta = \psi_d$) due to the electrical double layer compression. Earlier investigators [21] have pointed out that the changes in zeta potentials are directly reflected by surface modifications under high electrolyte concentration (10^{-2} mol l^{-1}).

The formation of surface complexes was examined qualitatively after extracting them into organic solvents and recording their UV–visible spectra. Pure copper dithiocarbamate complexes were prepared and their UV–visible spectra (Figs 6 and 7) compared with those of the surface products. Both Cu(I) DTC and Cu(DTC)$_2$ are soluble in CCl$_4$ and exhibit characteristic peaks at different wavelengths, whereas charged species like [Cu(DTC)]$^+$ are soluble only in polar solvents, in this case ethanol. By employing these two solvents separately it is possible to characterise all types of copper–DTC complexes. The broad peak observed at 435 nm is the characteristic peak of Cu(DTC)$_2$, and is attributed to the charge transfer between metal ion and ligand (M $\rightleftharpoons$ L). The other two peaks around 255 and 280 nm, with relatively sharp and high absorbance, are attributed to intraligand transitions such as n $\rightarrow$ σ^*, n $\rightarrow$ π^* and $\pi \rightarrow \pi^*$ [22]. Metal–ligand transitions in Cu(I) DTC and [Cu(DTC)]$^+$ are observed at a lower wavelength (385 nm) whereas mixtures of [Cu(DTC)]$^+$ and Cu(DTC)$_2$ in ethanol exhibit a very broad peak at 385–435 nm depending on the ratio of these com-

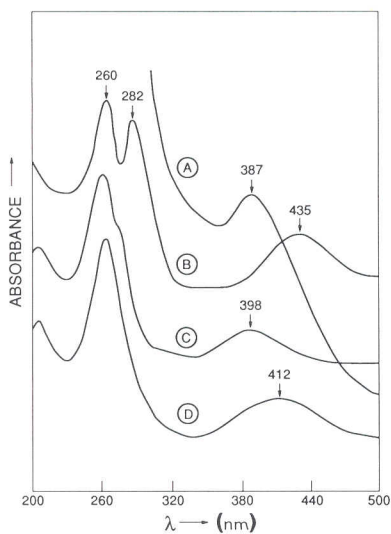Fig. 6. UV–visible spectra of Cu–DTC complexes in ethanol: (A) Cu(I) DTC; (B) Cu(DTC)$_2$; (C) [Cu(DTC)]$^+$; (D) mixture of (B) and (C).

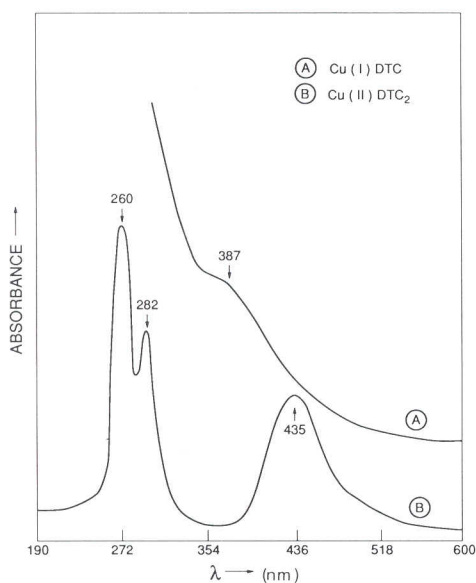Fig. 7. UV–visible spectra of (A) Cu(I) DTC and (B) Cu(DTC)$_2$ in CCl$_4$.

plexes [11]. The peaks that arise from intraligand transitions are merged into a single peak.

Figure 8 shows the UV–visible spectra of surface products ethanol-extracted from CuO equilibrated at various concentrations of DTC.
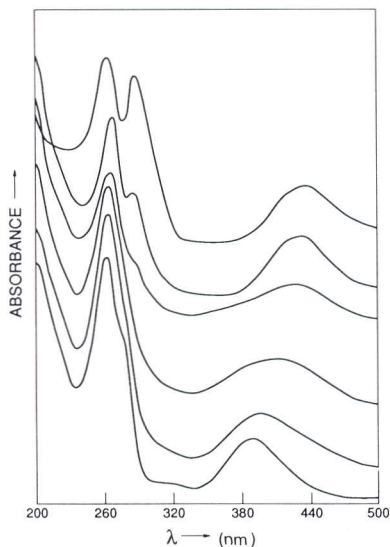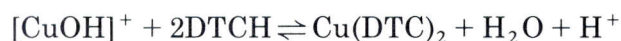
Fig. 8. UV–visible spectra in ethanol showing the effect of DTC concentration on surface complexation.

Surface products extracted at very low DTC concentrations, i.e. below $8.87 \cdot 10^{-6}$ mol l^{-1}, show a peak at 385 nm, confirming the formation of $[Cu(DTC)]^+$ on the surface. As the concentration of DTC increases, this peak shifts towards higher wavelengths, indicating the conversion of $[Cu(DTC)]^+$ into $Cu(DTC)_2$. Similar behaviour was observed with covellite. Thus the surface species extracted from CuO and CuS at different concentrations of DTC are in good agreement with those calculated thermodynamically. The solvent extraction technique is particularly useful and effective when a mixture of species are present in the system under study.

The nature of copper dithiocarbamate surface species on Cu_2O was also examined. At a very low concentration of DTC, surface species extracted with ethanol showed a peak at 385 nm. Since both $[Cu(DTC)]^+$ and Cu(I) DTC in ethanol exhibit a peak at about the same wavelength it is difficult to distinguish between these complexes in this solvent. However, it is possible to separate these two species by extracting with CCl_4, in which Cu(I) DTC is preferentially soluble. The CCl_4 extract showed a weak peak at 380 nm, confirming the existence of Cu(I) DTC at low DTC concentration. This suggests that complexes of Cu(I) DTC are stable in aqueous solution. Surface species at high DTC concentrations were found to be dominated by $Cu(DTC)_2$. It should be noted that Cu^+ ions dissolved from Cu_2O are highly unstable and disproportionate in water.

It is obvious that the dissolved metal ions from Cu_2O are in the form of Cu^{2+}. However, Cu^+ ions are stable as complexes with certain ligands. The dissolved metal ions from Cu_2O are oxidized to Cu^{2+} before complexing with DTC. The surface complexes $[Cu(DTC)]^+$ and $Cu(DTC)_2$ noticed on Cu_2O are a result of dissolved metal ions reprecipitated on the surface after reacting with DTC via $Cu(OH)_2$ or $[CuOH]^+$, whereas direct interaction of DTC with surface Cu(I) sites leads to Cu(I) DTC. Thus three types of surface species, i.e. Cu(I) DTC, $[Cu(DTC)]^+$ and $Cu(DTC)_2$, are possible on Cu_2O.

The effect of pH on the adsorption of DTC was studied on CuS and the results are plotted in Fig. 9. Adsorption densities are almost the same in the region $8.0 > pH < 10.0$. Slightly lower adsorption densities below pH 8.0 could be explained as being due to the protonation of DTC anion. Since the pK_a value of diethyldithiocarbamate is 7.5 [10], DTC^- is protonated below pH 7.5. Chemical interaction between copper species and the dithiocarbamate molecule is expected to proceed via deprotonation of the ligand, which can be represented as

$$DTC^- + H^+ \rightleftharpoons DTCH$$

$$Cu^{2+} + 2DTCH \rightleftharpoons Cu(DTC)_2 + 2H^+$$

$$[CuOH]^+ + DTCH \rightleftharpoons [CuDTC]^+ + H_2O$$

$$[CuOH]^+ + 2DTCH \rightleftharpoons Cu(DTC)_2 + H_2O + H^+$$

$$Cu(OH)_2 + 2DTCH \rightleftharpoons (Cu(DTC)_2 + 2H_2O$$

Low adsorption densities at higher alkaline pH could be explained

CONC. OF DTC : 8.876×10^{-4} mol/l
STIRRING SPEED : 1200 rpm
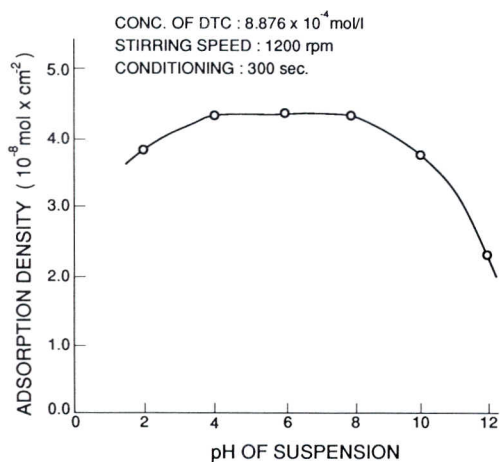CONDITIONING : 300 sec.

Fig. 9. Effect of pH on adsorption density.

as a competition between OH^- and DTC^- in the copper complexation reaction.

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

(1) diffusion of ligand molecules to the interface;
(2) adsorption at the interface;
(3) reaction at the interface;
(4) desorption of products;
(5) diffusion of products from the interface.

As a result of diffusion, adsorption and reaction of DTC with the mineral surface, a stagnant film (boundary layer) comprising the various surface complexes is formed around each particle. Hence the above reaction can be characterized as heterogeneous. Heterogeneous reactions can be either diffusion controlled, chemically controlled or intermediate controlled, depending on the slowest step, and further experiments were conducted to study the rate controlling process of the system. It was noted from Fig. 1 that the surface reactions are completed within the first five minutes, which therefore is the time limit for gathering kinetic data.

According to Fick's law [23], the rate equation for diffusion-controlled reactions can be expressed as

$$\text{Rate} = \frac{D}{\delta} A (C - C_i)$$

where C is the initial concentration of reagent; C_i is the concentration of reagent at the interface; D is the diffusion coefficient; δ is the thickness of the boundary layer; A is the surface area of the solid.

In diffusion-controlled reactions, the rate of chemical reaction at the interface is much faster than the rate of diffusion of the reactant into the interface. As a result, the concentration of the reagent at the interface will become zero. Hence the rate equation for diffusion-controlled reactions can be written as

$$\text{Rate} = K_1 A C$$

When a thick coating of Cu–DTC complexes is formed around the particle, the rate of chemical reaction will be much slower than the rate of diffusion. Under such conditions the adsorption of DTC is mainly controlled by the chemical process, the rate equation for which is given by

$$\text{Rate} = K_2 A C_i^n$$

Adsorption of DTC was followed with time at different initial concentrations of DTC; the initial adsorption rate was calculated from the tangents of these curves and the results are plotted in Fig. 10. The rate constant for a diffusion-controlled reaction (K_1) can be obtained from the slope of the straight line. The rate constant for a chemically controlled reaction (K_2) can be obtained by plotting the rate of the reaction calculated for the initial five minutes against the equilibrium concentration (concentration of the reagent at the interface) of the reagent (Fig. 11). The rate constants thus obtained for the CuO−DTC system were compared to describe the overall rate controlling process.
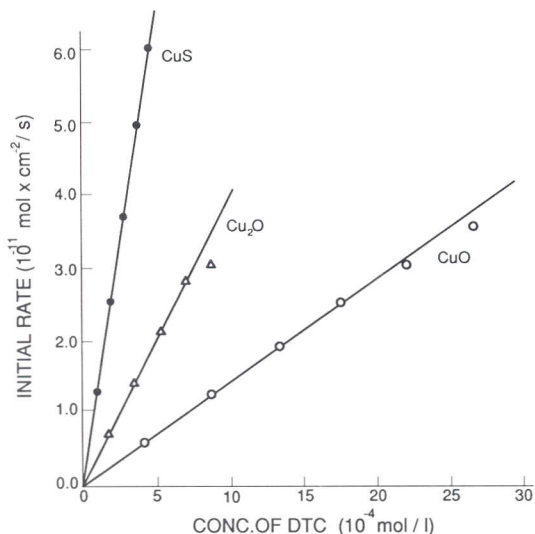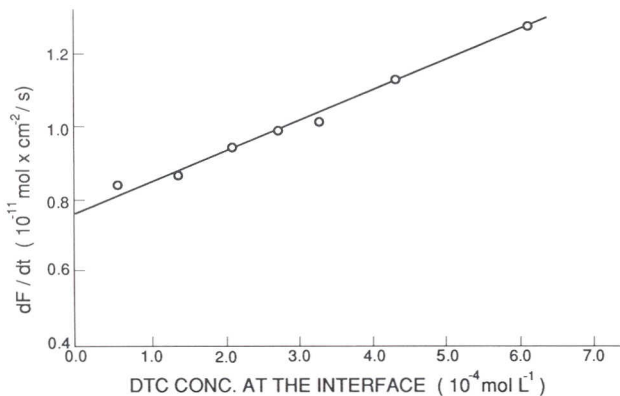

Fig. 10. Effect of DTC concentration on dF/dt.

Fig. 11. Plot of interfacial concentration of DTC versus dF/dt.

Since $K_1 = 2.68 \cdot 10^{-8}$ cm s^{-1} is less than $K_2 = 8.33 \cdot 10^{-8}$ cm s^{-1}, the overall process will be dominated by diffusion control. It should be noted that kinetic results provide very little information about the mechanism of chemical reaction when the rate is controlled by diffusion.

SUMMARY AND CONCLUSIONS

Adsorption behaviour of DTC on covellite, cuprite and tenorite was examined at different concentrations of DTC and pH of the suspensions. The results of this adsorption study indicate a surface reaction (chemisorption) mechanism whereby the cations are dislodged from the mineral surface when the DTC interacts either directly or through copper hydroxy complexes precipitated at the interface. It is possible to identify various copper–DTC complexes formed on the surface by selective solvent extraction and characterisation by UV–visible spectrophotometry.

Depending on the concentration of DTC, two types of surface species, i.e. $[Cu(DTC)]^+$ and $Cu(DTC)_2$, are possible on covellite and tenorite, whereas on cuprite Cu(I) DTC was formed along with $[Cu(DTC)]^+$ and $Cu(DTC)_2$. Initially, $[Cu(DTC)]^+$ species are formed at very low concentrations of DTC and are converted into $Cu(DTC)_2$ with increase in reagent concentration. The formation of $[Cu(DTC)]^+$ and its conversion into $Cu(DTC)_2$ was established by the resultant shifts in the UV–visible spectra of surface species and by zeta potential measurements.

From the kinetic study, the overall process of adsorption was found to be mainly controlled by diffusion process.

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