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Soluble Copper Xanthate Complexes

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Abstract

When solutions of cupric perchlorate (10^{-6} to 10^{-2} M) are mixed with solutions containing nonequivalent quantities (concentrations) of xanthate (*O*-alkyl-dithiocarbonate) ions, clear solutions containing soluble nonionic and ionic complexes are obtained, despite the fact that the solubility product for a given metal xanthate salt may be exceeded by several orders of magnitude. Ultraviolet and visible (UV and VIS) spectroscopy, and dc and ac differential polarography have been employed to study these complex species.

The spectral changes taking place on the addition of potassium ethyl xanthate to cupric perchlorate solutions, and also turbidity measurements, indicate that copper xanthate complexes are formed before the precipitation of cuprous ethyl xanthate, $Cu(S_2COC_2H_5)$. In very dilute solutions containing near-equivalent concentrations of the reactants, a spectrum containing three broad maxima (235, 285, and 375 nm) is obtained and is interpreted as due to a nonionic cupric complex, $Cu(S_2COC_2H_5)_2$, (I). In the presence of excess cupric ions a second complex, an ionized cupric monoxanthate, $Cu(S_2COC_2H_5)^+$, (II), is formed with bands at 256, 283, 325, and 382 nm. The relative concentrations of the reactants determine not only which complex is formed in these dilute solutions, but also whether or not the cuprous xanthate precipitates.

The species in solutions giving the spectrum of complex (I) is not stable. It decomposes quickly to cuprous xanthate and dixanthogen. Solutions of the

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ionic cupric complex (II) are stable for many hours. It is suggested that the ionic complex (II) may play a role in activating sphalerite in alkaline solutions.

INTRODUCTION

Alkyl xanthates (*O*-alkyl dithiocarbonates) are extensively used as collectors in the flotation of mineral sulfides (e.g., lead, zinc, copper, nickel). Infrared spectra of ethyl xanthate ($C_2H_5OCS_2^-$), hereafter denoted by (EtX^-), adsorbed on copper substrates have shown that cuprous xanthate, $Cu(S_2COC_2H_5)$, denoted by Cu(EtX), and dixanthogen, $(C_2H_5OCS_2)_2$, denoted by $(EtX)_2$, are present on the surface (*8*). It has been proposed that these are the species which are mainly responsible for the hydrophobic character of the surfaces of copper sulfide minerals. However, since oxidation of sulfides (during prolonged grinding) leads to the release of metal ions into the surrounding liquid phase, homogeneous reactions may also occur in the liquid phase between the metal ions and the collector species, and their products may influence the hydrophobic character of the mineral surface.

The reaction product of cupric salts with potassium ethyl xanthate has been studied extensively. The great majority of workers conclude that the yellow reaction product is a mixture of cuprous xanthate and dixanthogen (*4*, *12*). However, Solozhenkin and co-workers (*19*) have proposed, on the basis of ESR (electron spin resonance) spectra, that cupric xanthate is formed during the reaction. The aim of this work has been to confirm the existence of and to characterize the complexes which are formed in the solutions before the yellow reaction product precipitates.

Solubility studies on the formation of metal-surfactant precipitates by Matijevic et al. (*10*, *11*), and Nemeth and Matijevic (*14*) indicated that there are regions of nonequivalent concentrations in which stable dispersions of small particles exist, and others in which metal-surfactant complexes are formed in the solutions. Majima (*9*) and Yamasaki and Nanjo (*23*) reported on the formation of metal xanthate complexes in nonaqueous and aqueous solutions, respectively. Turbidity measurements made by Sheikh and Leja (*18*) on the mixed solutions containing cupric ions and xanthate ions, and those reported here (Fig. 1), indicated that metal xanthate complexes were present in the solutions during the precipitation reactions. The ultraviolet-visible (UV-VIS) spectral changes and dc differential polarograms taken during the reaction have been recorded. It appears that the relative concentration ranges of the reactants play a critical role in determining which complex is formed and whether or not the coarse precipitate is obtained.

EXPERIMENTAL

Materials

Copper perchlorate, $Cu(ClO_4)_2 \cdot 6H_2O$ (K and K Laboratories), was used as received. Potassium ethyl xanthate was prepared in the laboratory by reaction of ethanolic NaOH with CS_2 at ~10°C and recrystallized twice from acetone/diethyl ether. All other chemicals were of the highest purity. Solutions were prepared using double distilled water from an all-Pyrex still.

Spectroscopic Measurements

Infrared spectra were recorded with a Perkin-Elmer Model 521 grating infrared spectrophotometer. Spectra were recorded as of Nujol mulls between potassium bromide plates or as of potassium bromide disks.

Ultraviolet spectra were recorded with a Perkin-Elmer Model 450 NIR-Visible-UV spectrophotometer, using 10 cm cells (for very dilute solutions), 3 cm cells (for intermediate concentrations), and 1 cm matched quartz cells. Freshly prepared solutions of potassium ethyl xanthate were added into the solution of metallic salt, which was at the required pH, and the spectral changes recorded against water as a reference.

Turbidity Measurements

Turbidity measurements were made with a Brice-Phoenix Series 2000 Light Scattering Photometer at a wavelength of 436 nm. A semioctagonal dissymmetry cell 40 × 40 nm was used. The solutions were prepared by mixing, with stirring, equal volumes of potassium ethyl xanthate and copper perchlorate, or by diluting the potassium ethyl xanthate into a copper perchlorate solution, to obtain the desired concentrations. To allow a correlation with the spectral data, the values were recorded 15 min after mixing, even though the solutions may not have reached equilibrium.

Polarography Measurements

Polariter PO4 (Copenhagen) was used in polarographic measurements, using 0.2 M KNO_3 as supporting electrolyte, 10^{-3} M Cu^{2+}, and two concentrations of ethyl xanthate, 5×10^{-6} and 5×10^{-5} M. Polarograms were taken immediately after mixing and about 3 hr later.

RESULTS

CopperXanthate System

It has been known for many years that the particle size of the precipitate obtained when potassium ethyl xanthate is added to cupric salts depends on the concentration of the reagents (*6*). It is possible to produce a sol, which remains suspended for many hours, or a coarse precipitate, which rapidly settles out. Sheikh and Leja (*18*) have determined the concentration ranges of the reactants in which the coarse precipitate (Fig. 1, double hatched region) and the sol (Fig. 1, single hatched region) are obtained. However, they found that there is also a region in which no turbidity was observed, even though the solubility product of cuprous xanthate was exceeded by several orders of magnitude.

A more accurate determination of the turbidity of the solutions has now been made. The redetermined turbidity region extends slightly further to the low concentrations than the region indicated in 1974 by Sheikh and Leja (*18*). Despite this, however, there is still a region in which no precipitate was observed even though the solubility product of cuprous xanthate was exceeded. The shape of the solid line, the general solubility line, Fig. 1, indicates that some copper xanthate complexes are formed in the solutions containing a large excess of either component participating in the precipitation reaction.

Additions of a twofold excess of xanthate ions to dilute solutions of Cu^{2+} ($<10^{-5}$ *M*) yielded spectra with broad maxima at 235, 285, and 375 nm (Curve 1, Fig. 2). The spectra were not stable; the maximum at 375 nm slowly shifted to 410 nm, accompanied by the formation of a yellow sol. Similar spectra to that shown as Curve 1, Fig. 2, were also obtained at higher Cu^{2+} concentrations (10^{-4} to 10^{-5} *M*). However, the shift in the maximum at 375 nm (to give Curve 2, Fig. 2) and the concomitant sol formation were more rapid, being complete within 30 min.

The interpretation of these spectra and their changes is that the nonionized cupric complex $Cu(EtX)_2$ is formed initially in very dilute solutions. This complex is characterized by the band at 375 nm. It is unstable and decomposes readily to give a yellow sol containing cuprous xanthate, Cu(EtX), giving a band at 410 nm, and dixanthogen $(EtX)_2$, with bands at 235 and 285 nm. The change is the more rapid the higher is the concentration of reactants, particularly when the concentrations exceed those corresponding to the solubility product of Cu(EtX).

When the Cu^{2+} ion concentrations greatly exceeded the concentration

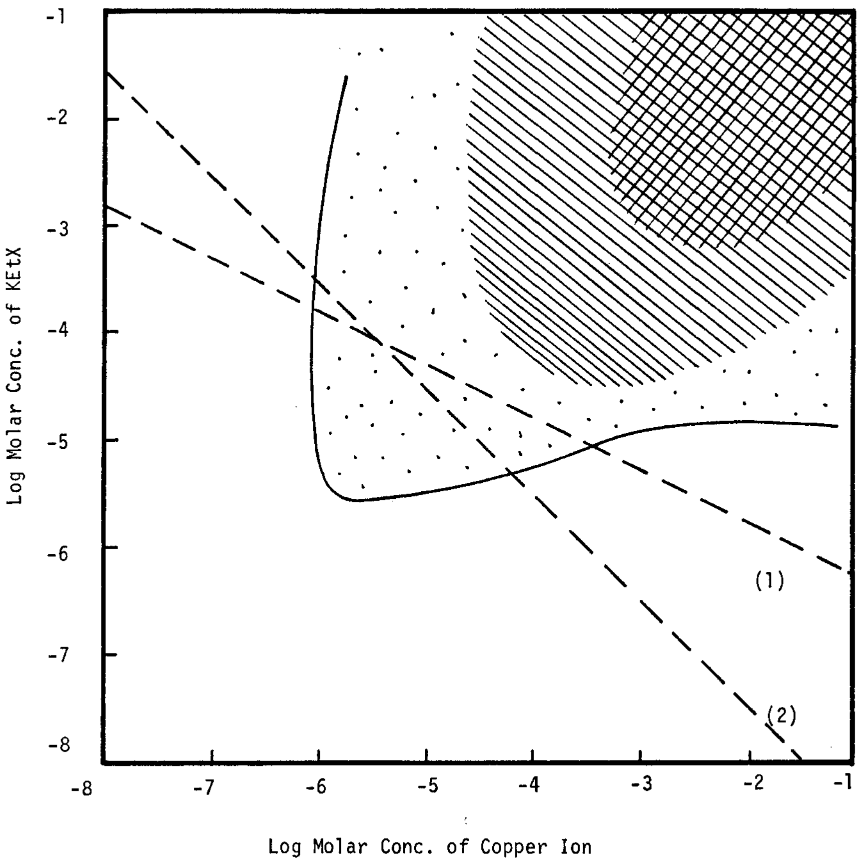

FIG. 1. Precipitation and complex formation regions for solutions of potassium ethyl xanthate and copper ion. Double-hatched region: *coarse-size precipitate* (formed immediately on mixing). Single-hatched region: very *fine size precipitate* or *sol*. Region of dots: invisible sol, detected by light scattering, formed immediately. Solid line: solubility line, experimental; below the solid line–complexes formed. Line (1): theoretical limits of solubility, $K_{sp} = (Cu^{2+})(EtX)^2 = 2 \times 10^{-14}$. Line (2): $K_{sp} = (Cu^+)^2(EtX)^2 = 5.2 \times 10^{-20}$.

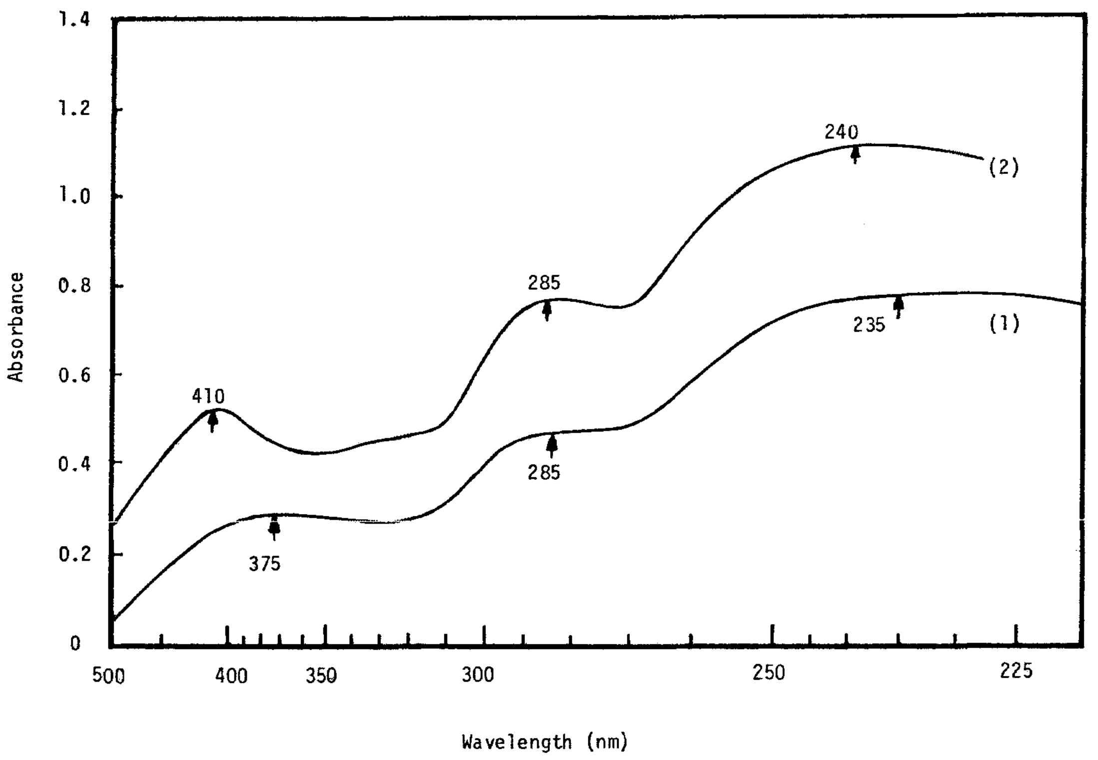

FIG. 2. UV spectra of the following solutions, 10 cm path length. Curve (1): $[Cu^{2+}] = 5 \times 10^{-6}$ *M*: [KEtX] = 10^{-5} *M*; initial spectrum. Curve (2): $[Cu^{2+}] = 4 \times 10^{-5}$ *M*; [KEtX] = 2×10^{-5} *M*; after 30 min.

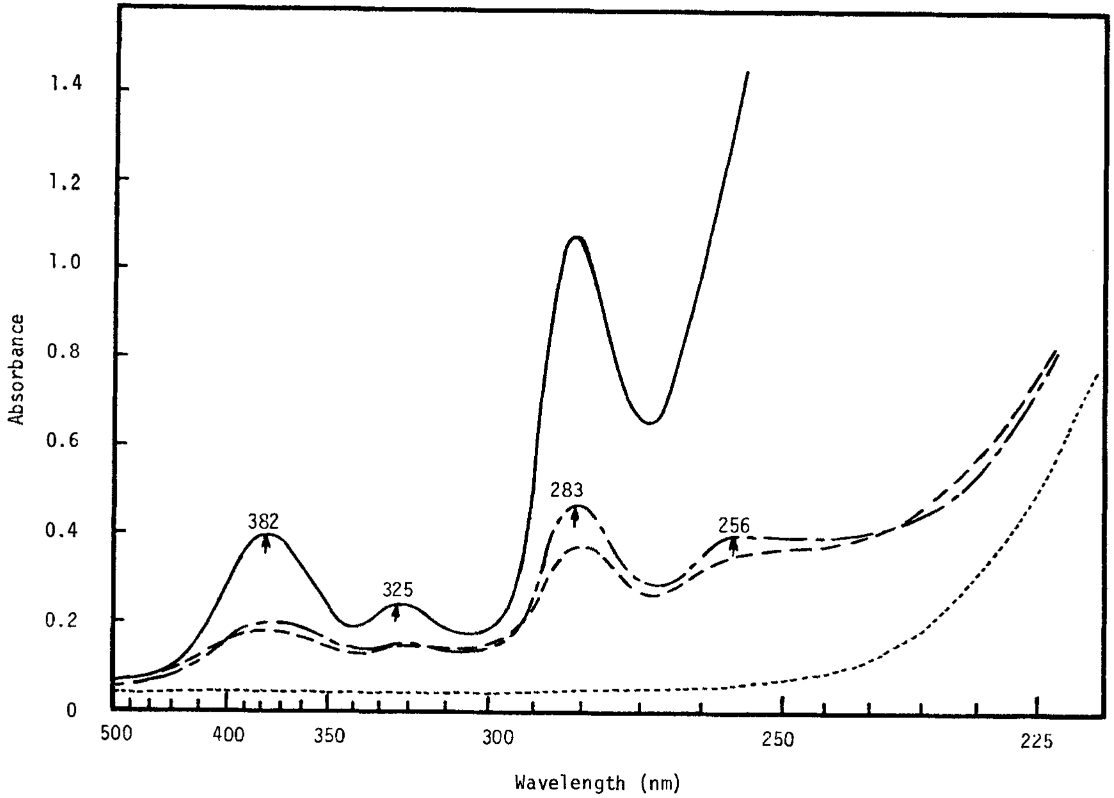

FIG. 3. UV spectra of the following solutions, 10 cm path length. (——): $[Cu^{2+}] = 10^{-2}$ M; [KEtX] $= 10^{-5}$ M; initial spectrum. (—-): $[Cu^{2+}] = 10^{-4}$ M; [KEtX] $= 5 \times 10^{-6}$ M; initial spectrum. (--): $[Cu^{2+}] = 10^{-4}$; [KEtX] $= 5 \times 10^{-6}$ M; after 60 min. (- -): $[Cu^{2+}] = 10^{-4}$ M; [KEtX] = nil.

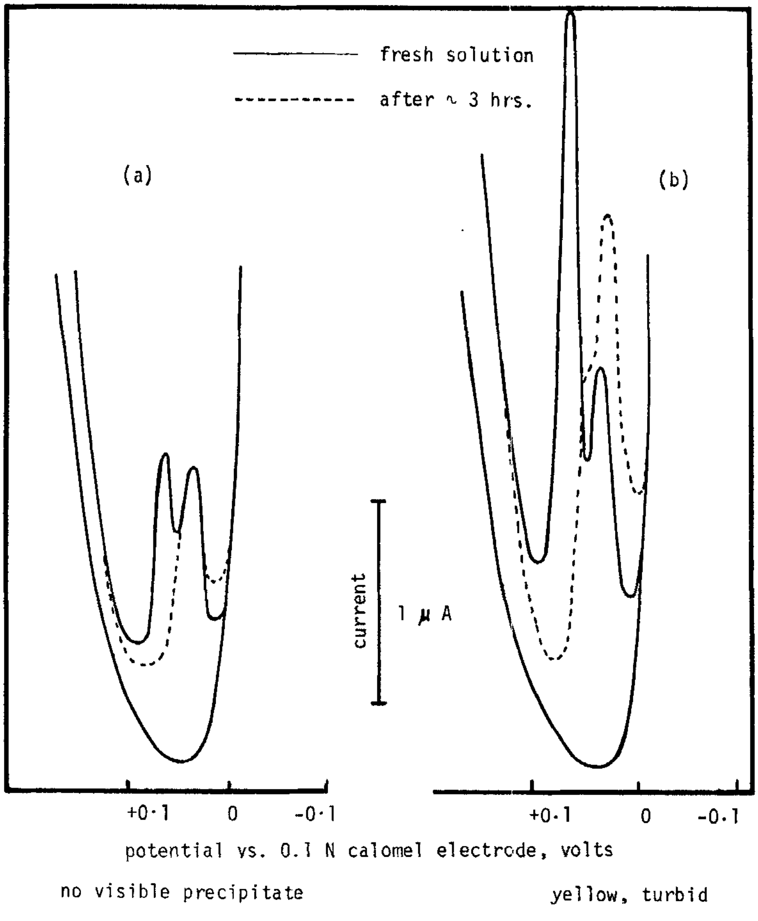

FIG. 4. Typical ac polarograms obtained/after mixing 0.2 M KNO_3 + 10^{-3} M Cu^{2+} solutions with (a) 5 × 10^{-6} M EtX^- solution and (b) 50 × 10^{-6} M EtX^- solution.

of xanthate ions, the spectra obtained showed maxima at 256, 283, 325, and 382 nm (Fig. 3). These were reproducible and stable (for 12 hr and more, without a change in the intensity of absorption), and were interpreted as due to the ionic cupric monoxanthate complex, $Cu(EtX)^+$. The intensity of the 283 nm peak decreases with time unless the excess of Cu^{2+} is greater than approximately 100-fold.

Figure 4 shows typical ac polarograms obtained immediately after mixing solutions of 10^{-3} *M* Cu^{2+} with 5×10^{-6} *M* EtX^- and with 5×10^{-5} *M* EtX^- (both containing 0.2 *M* KNO_3), shown as solid lines, and polarograms of the same mixed solution 3 hr later, shown as dashed lines. The maximum at +75 mV is seen to disappear with time in both mixtures with a concomitant increase in the +35 mV maximum (vs 0.1 *N* calomel electrode). These two maxima correspond to the two half-wave potentials of copper ion reduction from $Cu^{2+} \rightarrow Cu^0$ (+75 mV) and $Cu^+ \rightarrow Cu^0$ (+35 mV). Thus the ac polarograms show the initial nonionic cupric xanthate being decomposed to cuprous xanthate Cu(EtX) and dixanthogen $(EtX)_2$ in solutions of high ionic strength.

The spectra in Fig. 3 were obtained in solutions at their natural pH (5 to 6). In 0.1 *M* $HClO_4$ (pH = 1.8), similar spectra were recorded but with slightly lower intensity. An additional absorption band at 206 nm, due to CS_2, resulting from acid decomposition of excess xanthate, was often present. The spectra, characterized by maxima at 235, 285, and 375 nm [interpreted as cupric complex $Cu(EtX)_2$], were stable in the acid pH range, particularly when obtained with dilute reactant solutions.

When the pH of copper solutions (10^{-4} to 10^{-3} *M*) was adjusted to pH 9 or 10.5 (with KOH), a fine blue suspension of copper hydroxide was immediately converted to a yellow suspension on addition of xanthate solution. The spectra obtained within a minute of initiating the reaction showed a maximum at 400 to 410 nm, indicating the formation of cuprous xanthate. An infrared spectrum confirmed the presence of cuprous xanthate in the precipitate.

The procedure of pH adjustment was changed in that the 5×10^{-5} *M* KEtX solution was first mixed with 5×10^{-3} *M* $CuSO_4 \cdot 5H_2O$ solution and then the pH was adjusted to different values: (5.2), 6.0, 8.0, 9.5, and 11.0, using small quantities of KOH solution. The spectra obtained on clear solutions within 1 to 30 min of mixing showed peaks at 283, 300, 383, and 410 nm at various relative absorbances. The intensity of absorption changed if the solutions, containing some yellowish, green, or bluish precipitates (depending on pH), were intermittently shaken. Depending on the extent to which the precipitate was mixed with the yellowish-green solution, some peaks tended to disappear while others appeared. The disappearance of the peak at 410 nm was always accompanied by the appearance of a peak at 300 nm, due to EtX^-, at pH 11.0. The peak at 283 nm was not always clearly distinguishable when a 1-cm or a 3-cm path length was used, but could be easily seen in a spectrum obtained with a 10-cm cell.

DISCUSSION

The general solubility line for the copper xanthate system (Fig. 1, solid line) is not a straight line, as the solubility product would suggest, but is near-parabolic in shape. When the concentrations exceed those indicated by this line, sooner or later a yellow precipitate is formed. The IR spectrum of this precipitate confirmed that it represented a mixture of cuprous xanthate and dixanthogen. An UV spectrum of the solid (recorded as a suspension in a Nujol mull) was characterized by a maximum at 415 nm. Below 300 nm the scatter became too great and it was not possible to obtain reproducible spectra. In the reaction solutions the shift of the maximum in the range 385–365 to 410 nm (Curve 1 to Curve 2, Fig. 2) was always associated with the appearance of the yellow solid. Thus this absorption at 410 nm is assigned to cuprous xanthate, the maximum arising from the scattering of the beam by the colloidal-sized particles in the solution. This assignment is consistent with the decrease in the intensity of the absorption recorded as the solid agglomerated and settled out. The two maxima, 283 and 238 nm, associated with the absorption at 410 nm (Curve 2, Fig. 2) are due to dixanthogen.

The characteristic spectrum in Fig. 3 must be associated with copper xanthate complexes in the solutions. The maxima are in the regions expected for xanthic acid derivatives (*16*) and are not those of the free ethyl xanthate ion. Since the maxima of the spectrum in Fig. 3 have corresponding maxima in the spectrum in Fig. 2 (Curve 1), this suggests that the oxidation state of the metal is the same in both complexes. Both spectra were observed to be more stable in solutions which did not contain free xanthate (which may act as a reducing agent), and as cuprous complexes are known to be very insoluble, the two complexes whose spectra were recorded are proposed to contain the metal in the cupric state.

Yamasaki and Nanjo (*23*) have determined the solubility product constants for several metal xanthate systems. They also obtained stability constants for complexes formed in the solutions. Their calculations indicated that a 1:1 copper xanthate complex, $Cu(EtX)^+$, the cupric monoxanthate ion, was formed in the solutions. The complex with maxima at 256, 283, 325, and 382 nm (Fig. 3) is formed over a wide concentration range of an excess copper perchlorate. It is identical to that obtained by Yamasaki and Nanjo, and is formulated as the cupric monoxanthate ion. The peak at 283 nm is not due to the coexistence of dixanthogen.

The spectrum characterized by the maxima at 235, 285, and 375 nm (Curve 1, Fig. 2) could only be observed over a narrow and low concentration range, due to interference from excess xanthate and from the yellow sol. In the aqueous solutions the most stable spectrum was obtained when a twofold excess of the xanthate was used. This suggests that the complex contains two xanthate groups per metal ion and accordingly it is formulated as cupric xanthate, $Cu(EtX)_2$.

The shape of the general solubility line initially obtained by Sheikh (*17*) (Fig. 1, solid line) gave the first indication that complexes were formed in the solutions. At high concentrations of the cupric ions the shape of the general solubility line has now been shown to be due to the formation of the cupric monoxanthate ion in the solutions. Attempts to observe further complexes in the solutions containing excess xanthate ions were unsuccessful. When a solution of 30×10^{-6} *M* EtX^- (using a 3-cm cell) was mixed with a series of progressively increasing concentrations of Cu^{2+} (in 10^{-6} *M*), the sequence of spectra shown in Fig. 5 were obtained. Two isobestic points are clearly visible. The spectral changes are consistent with the reaction of Cu^{2+} with the xanthate ions (stoichiometry 1:2) to yield cuprous xanthate and dixanthogen.

It is unlikely that ionic cupric species such as $Cu(EtX)_3^-$ or $Cu(EtX)_4^{2-}$, similar to those observed in the cadmium system (*13*), will be formed by cupric species because of the reducing action associated with the excess xanthate. However, the solubility line indicates that some complexes must be formed in the high concentrations of xanthate ions. These may be cuprous anions, $Cu(EtX)_2^-$, etc.

The general solubility line determined here (Fig. 1) falls below the value of the solubility product for cuprous xanthate determined by Kakovsky (*7*). However, considering the number of reactions that have now been observed in the solutions, this is not unexpected.

The existence of complex copper xanthate species detected during precipitation suggests that the following reaction steps may be involved in acidic and near-neutral pH solutions:

$$n\mathrm{Cu}^{2+} + \mathrm{EtX}^- \rightleftarrows \mathrm{Cu(EtX)}^+ + (n-1)\mathrm{Cu}^{2+} \tag{1}$$

$$\mathrm{Cu(EtX)}^+ + \mathrm{EtX}^- \rightleftarrows \mathrm{Cu(EtX)}_2 \tag{2}$$

$$2\mathrm{Cu(EtX)}_2 \rightleftarrows 2\mathrm{Cu(EtX)} + (\mathrm{EtX})_2 \tag{3}$$

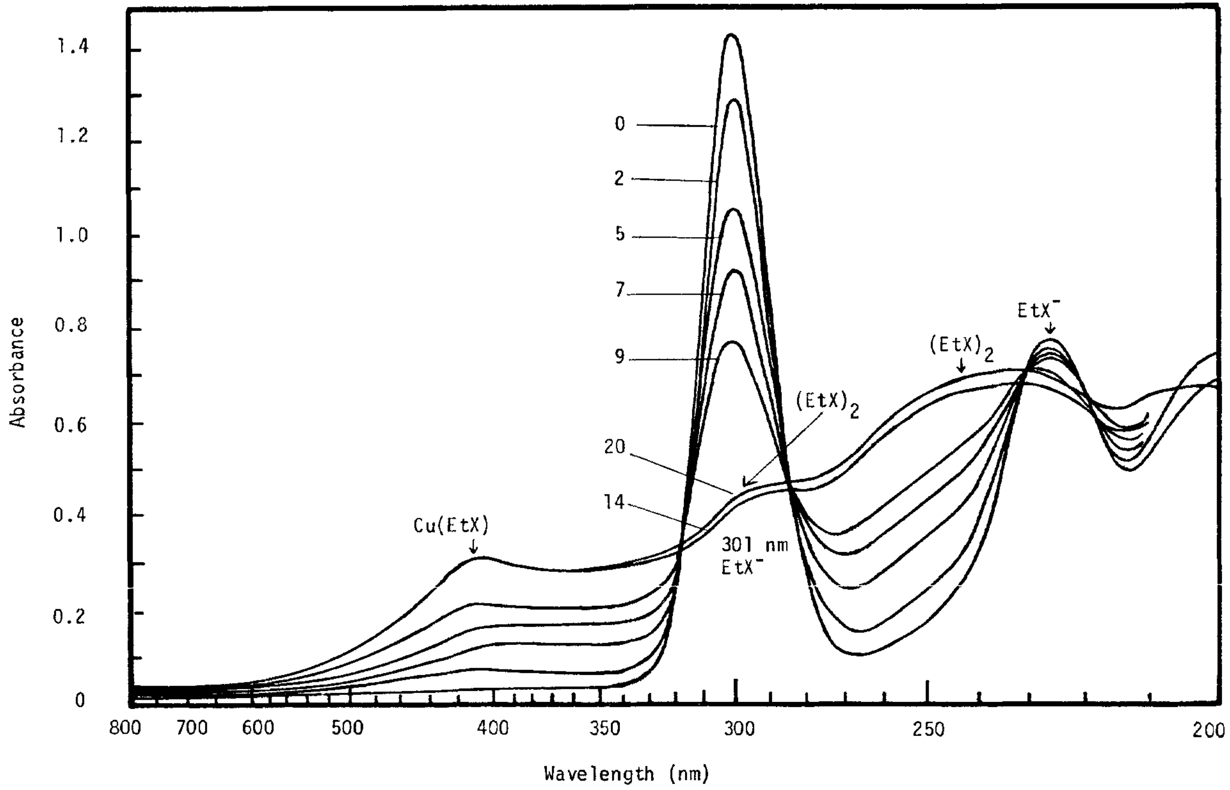

FIG. 5. The sequence of spectra obtained on mixing 0.2 *M* NaF + 30 × 10^{-6} *M* EtX$^-$ solution with 0 to 20 × 10^{-6} *M* Cu^{2+} solutions, 3 cm path length. The spectra are consistent with the precipitation of cuprous xanthate and dixanthogen.

and in high EtX^- concentrations

$$Cu(EtX) + EtX^- \rightleftarrows Cu(EtX)_2^- \tag{4}$$

Kinetically, the steps involving two-body collisions appear more probable than the reactions involving a three-body collision:

$$Cu^{2+} + 2EtX^- \rightleftarrows Cu(EtX)_2 \tag{5}$$

Depending on the relative concentration ratio of xanthate ions to cupric ions, the following stages of precipitation may predominate: the reaction Step (1) when Cu^{2+} ions are in ~10-fold to 100-fold excess; Step (2) when xanthate ions are in near equivalent amounts to Cu^{2+} and both are in very small concentrations; or Step (3) when either the concentrations are higher or longer times are allowed for the completion of reactions.

Reaction (1) is written in a form stressing the existence of an excess of Cu^{2+}. When the pH of the system is neutral or alkaline, this excess is involved in the formation of additional hydroxy complexes such as $Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, $Cu(OH)_2$, $Cu(OH)_3^-$, and $Cu(OH)_4^{2-}$, and carbonate complexes (in the presence of atmospheric CO_2) such as $CuCO_3$, $Cu(CO_3)_2^{2-}$, and $Cu(CO_3)_3^{4-}$. According to the data quoted by Steiniger (*20*), the solubility of $Cu(OH)_2$ in water is 5.5×10^{-5} *M*, and the dissociation constant of the dissolved $Cu(OH)_2$ is $K_d = 10^{-15.54}$:

$$Cu(OH)_{2(\text{aqueous})} \rightleftarrows Cu^{2+} + 2OH^- \tag{6}$$

The thermodynamic data for the whole range of copper mineral surface complexes mentioned above have also been reviewed by Attia (*1*). Unfortunately, there appears to be no agreement as to which of the complexes are the predominant ones at a given pH. For example, Attia's graphs show $Cu(OH)^+$ to predominate over $Cu_2(OH)_2^{2+}$ for all pH > ~5, whereas Steiniger claims that the potentiometric data indicate the opposite to be true. In addition to these uncertainties of thermodynamic data, the kinetics of reactions impose their limits on the predominance of species.

Possible Role of Complexes in Activation of Sphalerite by Copper for Flotation

In selective flotation of sphalerite, ZnS, which follows the removal of galena, PbS, by flotation with xanthate ions, an addition of $CuSO_4 \cdot 5H_2O$ is made to the mineral suspension, usually at pH > 9.0, for the purpose of activating sphalerite toward adsorption of xanthate species. It is presumed that a copper-containing species (unspecified) diffuses onto the sphalerite surface and exchanges thereon stoichiometrically with Zn^{2+} to form CuS. Gaudin (*3*) and Ralston et al. (*15*) confirmed the stoichiometric equivalence of Cu^{2+} uptake and Zn^{2+} release into solution in acidic pH regions. Steiniger (*20*) found that there was good flotation of sphalerite in solutions of pH less than 6 and in the alkaline region of pH > 9 but no flotation* between pH 6 and 9. Some narrowing of this no-floatability gap was observed by Steiniger depending on the relative quantities of EtX^- and Cu^{2+} added to the mineral suspensions of sphalerite.

Steiniger interpreted his flotation results in terms of complex basic copper xanthate formation, Cu(OH)EtX. He reasoned that below pH 6 there are insufficient OH^- ions to cause the complete removal of EtX^- by the formation of this complex. Above pH 9, $Cu(OH)_2$ precipitates, removing excess Cu ions that are required for the formation of this complex. In between these two limits, pH 6 to pH 9, the usual concentrations of Cu^{2+} to EtX^- ions are such that the Cu(OH)EtX complex is formed. The latter utilizes all available xanthate ions necessary for the adsorption on sphalerite, and thus causes sphalerite depression in flotation.

Girczys et al. (*5*) obtained flotation results similar to those of Steiniger. These they interpreted as activation of sphalerite caused by the precipitation of $Cu(OH)_2$ on the surface of sphalerite, and its subsequent reaction with EtX^- ions. Fuerstenau et al. (*2*) explained the floatability of chalcocite (Cu_2S) in the alkaline region by an analogous reaction of hydroxide on the chalocite surface:

$$Cu(OH)_{2(\mathrm{surface})} + 2EtX^- + 2H^+ \rightarrow Cu(EtX)_{(\mathrm{surface})} + \tfrac{1}{2}(EtX)_2 + H_2O \tag{7}$$

An IR spectrum of the product, obtained in the alkaline pH range after an addition of EtX^- to a $Cu(OH)_2$ precipitate was made, was similar to that of cuprous xanthate but also had a weak absorption assigned as a hydroxy stretching vibration. Copper hydroxides, *coprecipitated* with the product, may be responsible for this absorption or, as Steininger (*20*) has proposed, copper hydroxy xanthate, Cu(OH)EtX, may be formed in these solutions. These two possibilities have not, as yet, been resolved.

It is found in industrial practice that, for the best results in flotation of sphalerite, the addition of Cu^{2+} ions (as $CuSO_4 \cdot 5H_2O$) has to be invariably followed by an addition of xanthate ions. Otherwise no rapid flotation

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*This finding of Steiniger is not consistent with the practice in some Australian mills. See Woodcock and Jones (*22*).

will ensue. If an excess of xanthate ions is left after PbS flotation, the addition of Cu^{2+} causes their precipitation or complexation in a form which does not lead to a good flotation of sphalerite. The subsequent addition of xanthate that is required is an order of magnitude (or even two orders) smaller than the addition of Cu^{2+}. Xanthate is needed to make the sphalerite (presumably activated by Cu^{2+}) hydrophobic in character and floatable.

The surfaces of copper hydroxide (precipitated in the bulk solution or on sphalerite) and that of sphalerite in the absence of Cu ions in alkaline solution are negatively charged at $pH > 9$ due to an excess of OH^- ions adsorbed thereon. Yet, xanthate ions added to the copper hydroxide can convert the latter to the cuprous xanthate within a minute.

No direct UV-VIS spectroscopic evidence has been obtained to indicate the existence of a hydroxy complex, such as Cu(OH)EtX, suggested by Steiniger (*20*). This lack of evidence does not mean that such complexes do not or cannot exist. Simple ion pairing, such as

$$Cu(OH)^+ + EtX^- \rightleftarrows Cu(OH)EtX$$

may be expected to give a spectrum similar to that of the sum of the spectra of individual species. Another cause of an apparent lack of spectroscopic evidence may be due to the very high reaction rates of any intermediates which are formed. When no $Cu(OH)_2$ precipitate was present in the system, the spectra of clear solutions, in alkaline solutions at $pH < 11$, showed bands at ~283 and ~383 nm, indicative of $Cu(EtX)^+$ complex, at ~300 nm (due to EtX^-), and at 410 nm [due to soluble or very finely dispersed Cu(EtX)]. However, when the pH and Cu^{2+} ion concentration were such that $Cu(OH)_2$ formed an insoluble precipitate, the spectra indicated the presence of only EtX^- and CuEtX unless taken immediately after a thorough mixing of the system. This behavior seems to suggest that the $Cu(EtX)^+$ complex may be formed instantaneously and then immediately abstracted by the $Cu(OH)_2$ to yield the cuprous xanthate plus dixanthogen products. Even then, these two products are not the stable ones, but are decomposed by OH^-, as shown by Sheikh (*17*) and Tipman (*21*), and confirmed by a decrease in the 410 nm band and an increase in the EtX^- band at 300 nm, particularly at pH 11. It is obvious that the reaction in the $[Cu(OH)_2 + EtX^-]$ system and in the $[ZnS + Cu^{2+} + EtX^-]$ system are much more complex than hitherto visualized. A thorough study of the kinetics of different intermediate steps involved in the overall reaction of copper xanthate activation of sphalerite is desirable.

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REFERENCES

1. Y. A. Attia, *Trans. Inst. Min. Met.*, *84*, C221–230 (1975).
2. M. C. Fuerstenau, J. L. Huiatt, and M. C. Kuhn, *Trans. AIME*, *250*, 227–231 (1971).
3. A. M. Gaudin, *Ibid.*, *87*, 417–428 (1930).
4. A. M. Gaudin, F. Dewey, W. E. Duncan, R. A. Johnson, and O. F. Tengel, *Ibid.*, *112*, 319–347 (1934).
5. J. Girczys, J. Laskowski, and J. Lekki, *Can. Met. Q.*, *11*(4), 553–558 (1972).
6. W. J. Huff, *J. Am. Chem. Soc.*, *48*, 81–87 (1926).
7. I. A. Kakovsky, *Proceedings of the 2nd International Congress of Surface Activity*, Vol. 4, 1957, pp. 225–237.
8. J. Leja, L. H. Little, and G. W. Poling, *Trans. IMM*, *72*, 407–423 (1963).
9. H. Majima, *Sci. Rep. Res. Inst.*, *Tohoku Univ.*, *Ser. A*, *13*, 183–196 (1961).
10. E. Matijevic, J. P. Kratohvil, and M. Kerker, *Chem. Educ.*, *38*, 397–399 (1961).
11. E. Matijevic, J. Leja, and R. Nemeth, *J. Colloid Interface Sci.*, *22*, 419–429 (1966).
12. M. P. Matuszak, *J. Am. Chem. Soc.*, *53*, 4451–4452 (1931).
13. M. Nanjo and T. Yamasaki, *Sci. Rep. RITU*, *A21*, 33–44 (1969).
14. R. Nemeth and E. Matijevic, *Kolloid Z. Z. Polym.*, *245*, 497–507 (1971).
15. O. C. Ralston, C. R. King, and F. X. Tartaron, *Trans. AIME*, *87*, 389–400 (1930).
16. M. L. Shankaranarayana and C. C. Patel, *Acta Chem. Scand.*, *19*, 1113–1119 (1965).
17. N. Sheikh, Ph.D. Thesis, University of British Columbia, 1972.
18. N. Sheikh and J. Leja, *J. Colloid Interface Sci.*, *47*, 300–308 (1974).
19. P. M. Solozhenkin, N. I. Kopitsya, and K. T. Poroshin, *Dokl. Akad. Nauk SSSR*, *181*, 1440–1443 (1968).
20. J. Steiniger, *Trans. AIME*, *241*, 34–42 (1968).
21. N. R. Tipman, Ph.D. Thesis, University of British Columbia, 1970.
22. J. T. Woodcock and M. H. Jones, *Proc. Aust. Inst. Min. Met.*, *235*, 45–60 (1970).
23. T. Yamasaki and M. Nanjo, *Sci. Rep. RITU*, *A21*, 45–62 (1969).

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