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The Relation of Collector Redox Potential to Flotation Efficiency: Monothiocarbonates

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Abstract

The redox potentials of monothiocarbonates and xanthates have been determined and a correlation established with their collector properties for the flotation of galena. Flotation efficiency increases with the ease of oxidation of the collector. The role in flotation of the oxidation products, the disulfides, is discussed.

INTRODUCTION

The mode of action of xanthate collectors has been the subject of numerous investigations utilizing physical, chemical, and electrochemical techniques. The present state of knowledge has been recently presented in a critical review by Granville et al. (*1*).

The ability of a collector to impart the desired changes to the surface of the particle to be floated must ultimately depend on the collector's physical properties. This, in turn, must largely be dependent on the functional groups in either the collector itself or its reaction products. A systematic study, following classical principles, has been undertaken by us to study the effect of varying some of the functional groups in conventional xanthate collectors. We have already reported (*2*) the effects observed when a second xanthate group is introduced into the molecule to yield dixanthates. As a further modification, we have replaced one of the sulfur atoms of the xanthate group by oxygen to form monothiocarbonates. It is the purpose of the present communication to examine the effects of this modification.

Monothiocarbonates were first made in 1868 by Bender (*3*) and are frequently referred to as Bender's salts. Their possible use as flotation collectors for sulfides has received little attention. Wark and Wark (*4*) suggested that they had potential for use as collectors. Klassen and Mokrousov (*5*) also make reference to work of Kakovsky, who investigated monothiocarbonates and reported a lower collector efficiency as compared to xanthates.

METHOD AND RESULTS

The potassium methyl-, ethyl-, *n*-butyl-, *n*-amyl-, and *n*-hexyl monothiocarbonates were prepared by the insertion reaction of carbonyl sulfide into the potassium alkoxide of the appropriate alcohol. They are water-soluble crystalline compounds that slowly decompose on prolonged storage.

In the IR spectrum these compounds exhibit a characteristic absorption band at 1600 cm^{-1} due to the C=0 vibration. In the UV region they absorb at 222 nm ($\varepsilon = 10.3 \times 10^3$), as shown in Fig. 1, and this differentiates them from the xanthates which absorb at 301 nm ($\varepsilon = 17.5 \times 10^3$).

By analogy with the oxidation of xanthates to yield "dixanthogen" (Eq. 1), monothiocarbonates may be oxidized to the corresponding disulfide (Eq. 2). For this group of compounds we suggest the trivial name "carbonate disulfides."

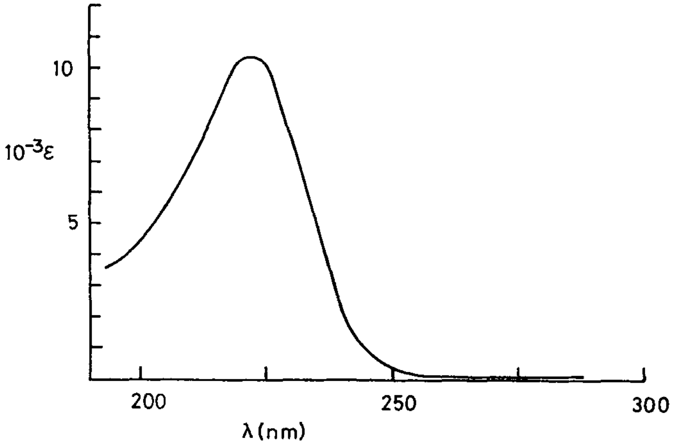
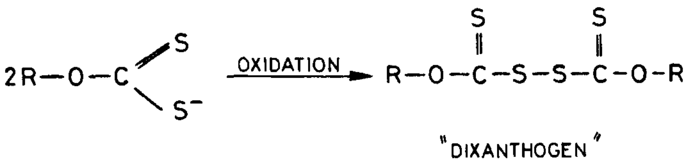
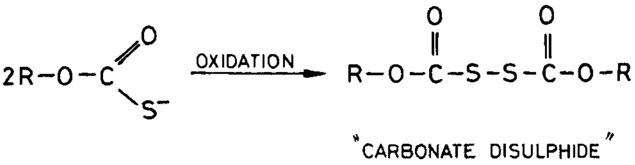


FIG. 1. Ultraviolet spectrum of ethyl monothiocarbonate.



$$2R{-}O{-}C\genfrac{}{}{0pt}{}{\diagup\!\!\!\diagup S}{\diagdown S^-} \xrightarrow{\text{OXIDATION}} R{-}O{-}\overset{\overset{S}{\|}}{C}{-}S{-}S{-}\overset{\overset{S}{\|}}{C}{-}O{-}R \qquad (1)$$



$$2R{-}O{-}C\genfrac{}{}{0pt}{}{\diagup\!\!\!\diagup O}{\diagdown S^-} \xrightarrow{\text{OXIDATION}} R{-}O{-}\overset{\overset{O}{\|}}{C}{-}S{-}S{-}\overset{\overset{O}{\|}}{C}{-}O{-}R \qquad (2)$$

We have isolated the carbonate disulfides by oxidation of the corresponding monothiocarbonates with potassium persulfate followed by extraction with ether. With the exception of the methyl compound which is a crystalline solid at room temperature, the carbonate disulfides are oily liquids that may be distilled under reduced pressure. In the IR spectrum they exhibit sharp absorption bands at 1720 and 1760 cm^{-1} (the latter band is sometimes split). These bands are in the region where absorption by a ketonic $C{=}0$ would be expected (see Fig. 2).

A more detailed account of the chemistry of monothiocarbonates will be published elsewhere.

The redox potentials for the monothiocarbonate/carbonate disulfide couples were determined potentiometrically using a platinum indicator electrode. Potentials were measured in 0.005 M sodium borate containing 10^{-2}, 10^{-3}, or 10^{-4} M of the monothiocarbonate with a layer of the disulfide present on the electrode surface. Solutions were deoxygenated with purified nitrogen. The reference electrode was a saturated calomel;

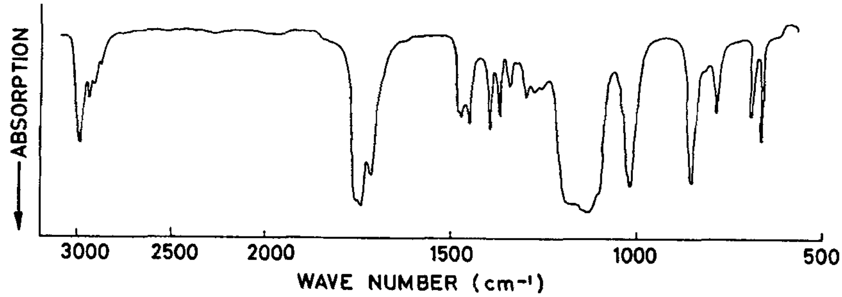


FIG. 2. Infrared spectrum (KBr disk) of ethyl carbonate disulfide.

TABLE 1

Comparison of Monothiocarbonate and Xanthate Redox Potentials with Flotation Efficiency for Galena[a]

	Monothiocarbonate			Xanthate	
Alkyl group	E° (V)	Flotation recovery (%)		E° (V)	Flotation recovery (%)
Methyl	+0.020	5	10[b]	−0.004	6
Ethyl	+0.002	10	95[b]	−0.057	88
n-Propyl	−0.022	n.d.		−0.090	93
n-Butyl	−0.038	20		−0.128	95
n-Amyl	−0.080	93		−0.158	n.d.
n-Hexyl	−0.120	95		n.d.	n.d.

[a] Collector concentration 10 ppm; pH 8.4 (8.5 g/l $NaHCO_3$).
[b] With 10 ppm Cu^{2+}.

potentials are reported against the standard hydrogen electrode assuming this to be −0.244 V relative to the calomel electrode. The E° values were obtained using the Nernst equation, taking the activity of the disulfides to be unity for each measurement. The values obtained from each concentration agreed within 2 mV. The results are listed in Table 1, which for comparison purposes also includes the corresponding potentials found for the homologous series of xanthates. The latter agree closely with values previously reported (*6*).

As with the xanthates, the E° of the monothiocarbonate/disulfide couple becomes progressively more negative with increasing chain length. This phenomenon cannot be ascribed to the inductive effect of the methyl group, which terminates the alkyl chain, since this would be expected to be negligible for chain lengths greater than three carbon atoms. Furthermore, it was found that there was no significant difference between the E° values of *n*-propyl and isopropyl xanthate (−0.090 and −0.089 V, respectively), indicating that the inductive effect is not important. The progressive change in E° values is mainly due to the choice of the standard state for the oxidized species. The overall oxidation reaction is from an aqueous thio-ion to a deposited neutral solid or liquid disulfide, and the overall free energy includes a contribution from the free energy of dissolution (i.e., the solubility) of the disulfide. Therefore, when the standard state of the disulfide in the Nernst equation is taken as unity for a separate phase, the E° will be affected by the solubility of the oxidized product. Indeed, Kakovsky and Arashkevich (*7*) have observed differences in the

TABLE 2

Collector Properties of Disulfides for Galena

Disulfide	Flotation recovery (%)
Ethyl dixanthogen	80
Methyl carbonate disulfide	40
Ethyl carbonate disulfide	90
Butyl carbonate disulfide	90

[a] Collector concentration 10 ppm deposited on mineral surface by evaporation from alcoholic solution; pH 8.4 (8.5 g/l $NaHCO_3$).

solubility of the oxidation products of xanthates and dithiophosphates, and concluded that they account for the changes in E° with alkyl chain length.

The collector properties of monothiocarbonates and disulfides were examined using a small Hallimond tube. The mineral investigated was galena (hand-picked specimens from the mine of The Zinc Corporation Ltd., Broken Hill, N.S.W.) ground to 100–150 mesh. The results are shown in Tables 1 and 2. The flotation recoveries are for a 2-min float under constant conditions.

DISCUSSION

Attachment of a mineral surface to an air bubble is brought about by collector molecules which, in general, consist of a hydrophobic nonpolar group plus a polar group capable of interaction with the mineral surface. It is the nonpolar group that has the main influence on the state of the surface when adsorption is a maximum. For example, Sutherland and Wark (*8*) demonstrated that, provided interaction with the surface took place, the maximum contact angle for a series of thio collectors was dependent only on the alkyl group, being independent of the polar group and of the mineral investigated.

In comparing the effects of changing the chemical nature of the polar group, the collector-mineral interaction is often considered, either explicitly or implicitly, to be one of ion adsorption. For example, Klassen and Mokrousov (*5*) state that monothiocarbonates and xanthates adsorb as negatively charged ions and that the decreased collecting action of the former compounds is due to a preferential interaction of the carbonyl group with water. However, it is now generally accepted (*1*, *6*, *9–12*) that the interaction of thio collectors with metals and sulfide minerals involves an oxidation reaction to form either a metal-collector species, an oxidized collector species, or a combination of both. In this case a correlation between the ease of oxidation of the collector and flotation is to be expected, the more readily oxidizable species being the more efficient. A convenient parameter for comparing collectors is the redox potential of the thio-ion/disulfide couple. It is to be expected that for related compounds the order of the potentials for heavy-metal compound formation will, in general, be parallel to such redox potentials.

There is a clear correlation between flotation recovery of galena and the redox potentials of the monothiocarbonates. As the alkyl chain length increases, the redox potential becomes more negative (Table 1), and hence the compounds are more easily oxidized, leading to more efficient flotation. Xanthates behave similarly in this regard. Increase in alkyl chain length also increases the maximum contact angle (*8*), but the difference between the monothiocarbonates and xanthates with the same alkyl group shows that this is not the important factor in increasing flotation efficiency.

The importance of the ease of oxidation of the collector is further substantiated by the observation that the oxidation products themselves are good collectors even under conditions where the corresponding monothiocarbonates are not (Tables 1 and 2). Thus the use of the disulfide renders oxidation with oxygen in the flotation system unnecessary. On this basis the addition of a mild oxidant such as Cu^{2+} would be expected to result in greater efficiency of the collector, and this is in fact observed (Table 1).

The oxidation product of methyl monothiocarbonate is obviously a poor collector, as shown by its performance in the Hallimond tube experiments. This may be connected with its physical properties, which are different from the rest of the series, since it alone is a crystalline solid whereas all other disulfides are oily liquids.

Flotation efficiency is affected by pH for a number of reasons. At high pH adsorbed compounds may be decomposed or replaced by hydroxyl. A decrease of pH will not only reduce these effects but will cause an increase in the ease of oxidation of the collector, although the redox potential of the collector is independent of pH. This is because the potential of the oxygen reduction process decreases by 59 mV for each pH unit. Hence the resultant mixed potential for a solution containing both collector and oxygen will become more favorable for collector oxidation as the pH is lowered. Therefore pH not only affects adsorption of the collector but also affects the ease of oxidation to the disulfide. Both are complementary and are beneficial to the efficiency of the collector. An increase in flotability with decrease in pH is observed for xanthates (*8*), and preliminary investigations have shown analogous behavior to occur for the monothiocarbonates. As the pH is decreased still further, the competing decomposition reaction of the collector results in loss of efficiency.

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