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Mössbauer Spectroscopy of Fe Xanthates*

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Abstract

Mössbauer spectroscopic studies indicate that, depending on pH, two different precipitates are formed when appropriate solutions of iron ions are mixed with ethyl xanthate solutions. Below pH 3.5, ferric ethyl xanthate is obtained, regardless of whether ferric or ferrous reactants are used; ferrous xanthate can be obtained only with highly concentrated solutions and in strictly neutral or even reducing conditions. Above pH 3.5 a ferric hydroxyxanthate, with one or more OH groups replacing the xanthate groups, is formed. No analogy with the $Cu^{2+} \rightarrow Cu^{+}$ reduction and the accompanying stoichiometric oxidation of xanthate to dixanthogen could be observed in the $Fe^{3+} \rightarrow Fe^{2+}$ systems, in which dixanthogen is detected only as a product of ferric xanthate decomposition in alkaline pH's.

INTRODUCTION

In the concentration of minerals by flotation, *O*-alkyl dithiocarbonates—known as xanthates—are commonly used for the purpose of converting the metallic sulfide minerals present in the feed from hydrophilic to hydrophobic in order that these mineral particles attach to air bubbles. The variety of chemical reactions involved in adsorption of xanthates on

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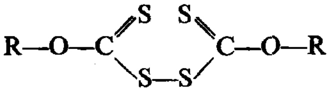
sulfides is far greater than suspected at the time when xanthates were first used (in 1925).

When a layer of adsorbed collector in a mineral–sulfide–xanthate flotation system is examined by IR spectroscopy, the spectra obtained indicate that the layer consists of one, two, or sometimes three different constituents (*1*). In PbS–xanthate systems, the first molecule of xanthate is adsorbed as Pb:X, a 1:1 coordinated complex which cannot be readily displaced by solvents that remove the co-adsorbed PbX_2 and X_2; the last constituent, dixanthogen, may be present under highly oxidizing conditions [X stands for an alkyl xanthate group, $C_nH_{2n+1}OCS_2^-$, X_2 for dixanthogen



where $R = C_nH_{2n+1}$].

In the case of copper minerals, IR spectra indicate Cu_2X_2 (cuprous xanthate) and X_2 (dixanthogen) coadsorbed on minerals (*2*). The metal xanthates coadsorbed on the surfaces of minerals appear to be precipitated from the excess M^{m+} in the electrical double layer surrounding the surface and derived from the partial dissolution of the mineral during contact with water. With Cu^{2+} ions the addition of X^- results in a reduction of Cu^{2+} to Cu^+ and an equivalent oxidation of X^- to X_2, giving a stoichiometric mixture of Cu_2X_2 and X_2 instead of the expected CuX_2 precipitate. This particular case of simultaneous reduction of metal ion and oxidation of xanthate ion to dixanthogen has been well documented by now, using chemical analysis [carried out for the first time by Gaudin and his coworkers (*3*) in 1934], IR, ESCA, and electron paramagnetic resonance (EPR). The last technique appears to give discordant results (*4*), but this is apparently due to superficial oxidation during sample preparation (*5*). A more detailed account of copper xanthate behavior in solution has been presented by Sparrow et al. (*6*).

Since iron in solution is capable of existing also in two oxidation states (Fe^{2+} and Fe^{3+}), it may be assumed that similar reduction from the Fe^{3+} to the Fe^{2+} state and precipitation of FeX_2, with simultaneous oxidation of a stoichiometric quantity of X^- to X_2, occurs in systems where iron sulfides are being floated. Unfortunately, there are no sufficiently selective organic solvents available (as is the case with the copper xanthate system) that would enable separation of X_2 from iron xanthate and an independent evaluation of the composition of the separated products. Further, IR spectra of iron xanthate, Fig. 1, have very similar absorption peaks to those

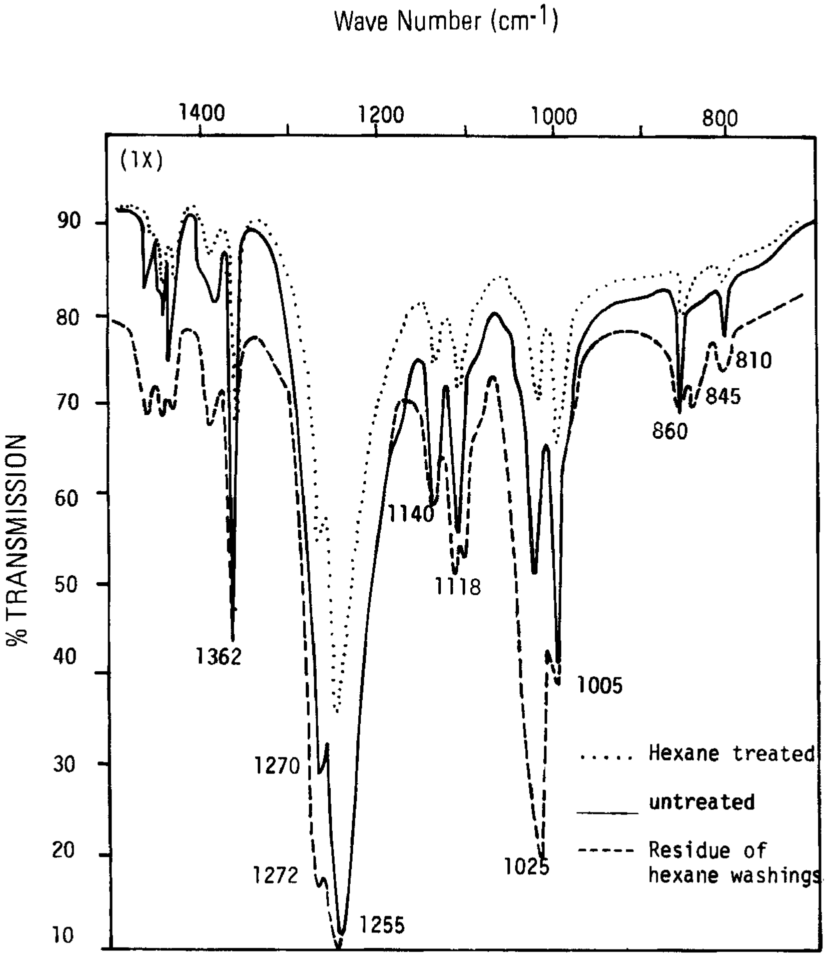


Fig. 1. The IR spectra of ferric ethylxanthate (untreated and treated with hexane) compared with the residue which remained upon evaporation of the hexane extracts. The ferric ethylxanthate was prepared at pH 3.5 and 25 °C.

in the spectrum of dixanthogen (main peaks in Fig. 5 solid line spectrum), while chemical analysis of iron xanthates precipitated in neutral solutions suggests that only two xanthate groups exist with one Fe. Hence the role of dixanthogen in flotation of pyrite (7) cannot be evaluated in a straightforward manner.

EXPERIMENTAL

The instrument used for recording of the Mössbauer spectra was a Technical Measurements Corporation Model 306 (kindly made available by Prof. J. Sams, Department of Chemistry, UBC), equipped with a ^{57}Co source (14.4 keV) which was moved by a transducer at a constant rate of acceleration. The transmitted γ-radiation was detected by a xenon-nitrogen proportional counter. The source and drive were calibrated against a single crystal of sodium nitroprusside.

The data were fitted by a computer to a Lorentzian-shaped absorption peak by a nonlinear least-square technique. The quadrupole splitting for the reference material was taken to be 1.726 ± 0.002 mm/sec. Isomer shifts were reported relative to the center of the spectrum of the standard. A 1-mm cell with Mylar windows contained the powdered sample.

A number of iron xanthate precipitates were obtained, under slightly different experimental conditions, on mixing 10^{-2} *M* solutions of potassium ethyl xanthate and ferric ammonium sulfate each at appropriate pH, as listed in Table 1. Mössbauer spectra were then recorded for these

TABLE 1
Sample Preparation of Ferric Ethylxanthate and Related Compounds

	Before mixing					
	Xanthate		Iron			
Sample no.	Conc (mole/liter)	pH	Conc (mole/liter)	pH	pH after mixing	Experimental conditions
1	10^{-2}	8.5	10^{-2} Fe^{3+}	2.5	2.7	Mixing in isolator box under N_2
2	10^{-2}	8.5	10^{-2} Fe^{3+}	2.5	2.7	Mixing in open atmosphere
3	10^{-2}	8.5	10^{-2} Fe^{3+}	2.5	2.7	Hexane washed precipitate
4	10^{-2}	2.7	10^{-2} Fe^{3+}	2.5	2.6	Mixing in open atmosphere
5	10^{-2}	7.0	10^{-2} Fe^{3+}	4.0	6.2	Floated part of precipitate
6	10^{-2}	7.0	10^{-2} Fe^{3+}	4.0	6.2	Sink part of precipitate
7	10^{-2}	8.5	10^{-2}	2.5	2.75	Four week old compound
8	1 *M*	7.5	1 *M* Fe^{2+}	3.6	6.1	In open atmosphere
9	1 *M*	7.5	1 *M* Fe^{2+}	3.6	6.2	In partially controlled atmosphere
10	1 *M*	7.5	1 *M* Fe^{2+}	3.6	6.3	In isolator box under N_2

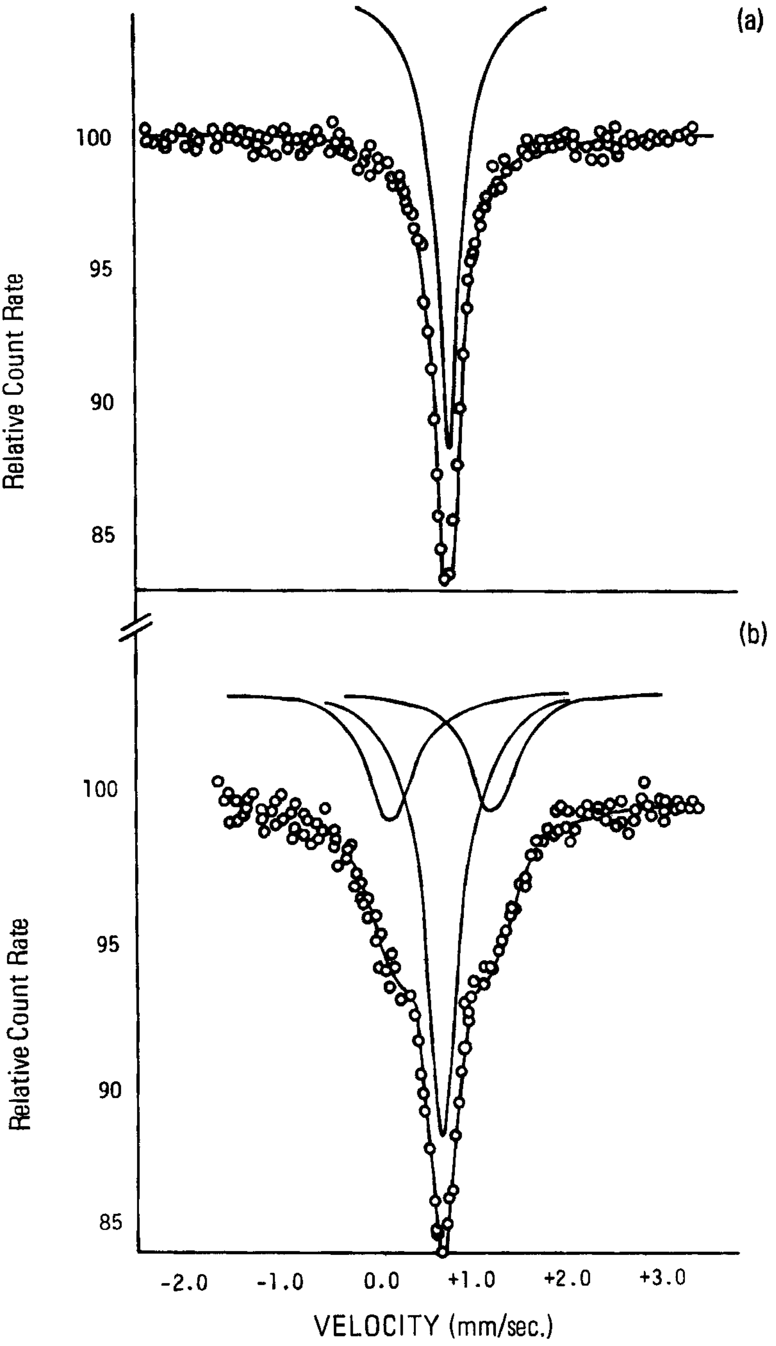


FIG. 2. Mössbauer spectra of ferric ethylxanthate, Fe(ROCS$_2$)$_3$. Spectrum (a) represents Samples 1–4 and Spectrum (b) is Sample 7 in Table 1.

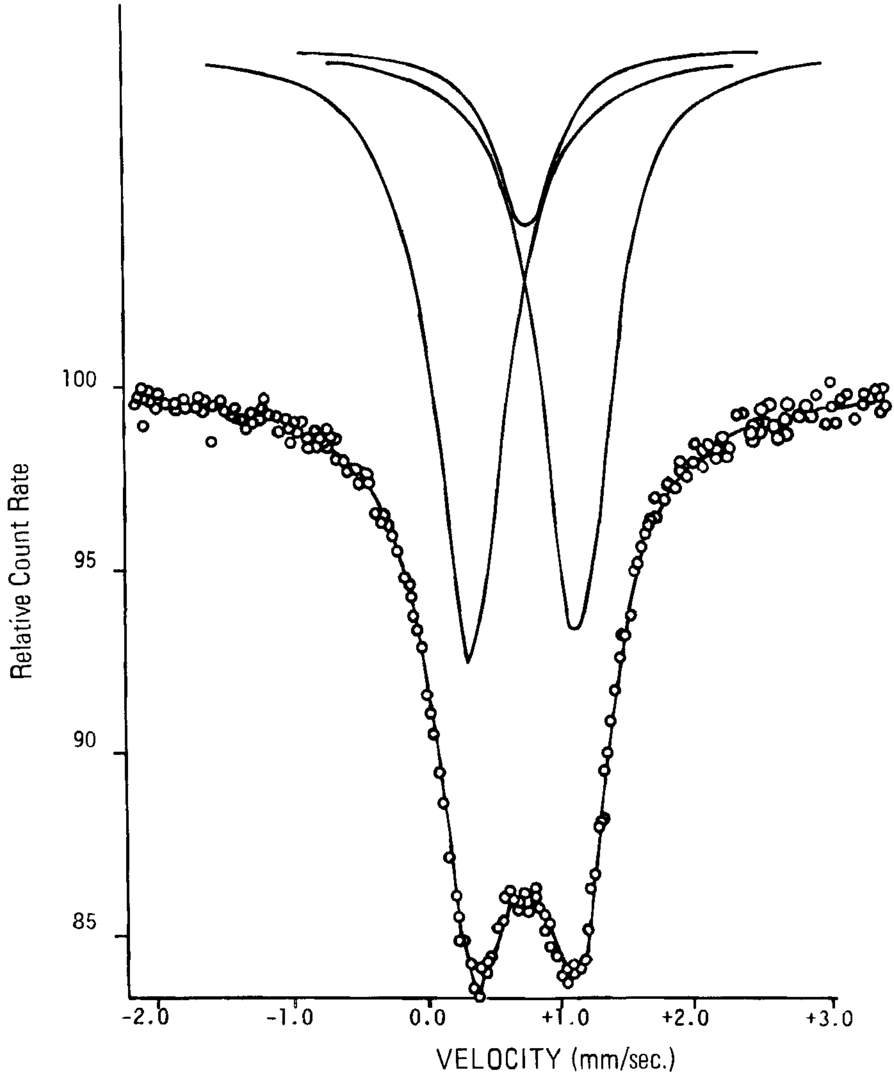


FIG. 3. Mössbauer spectrum interpreted as that of ferric hydroxy ethylxanthate, $Fe(OH)(ROCS_2)_2$ (Sample 6 in Table 1).

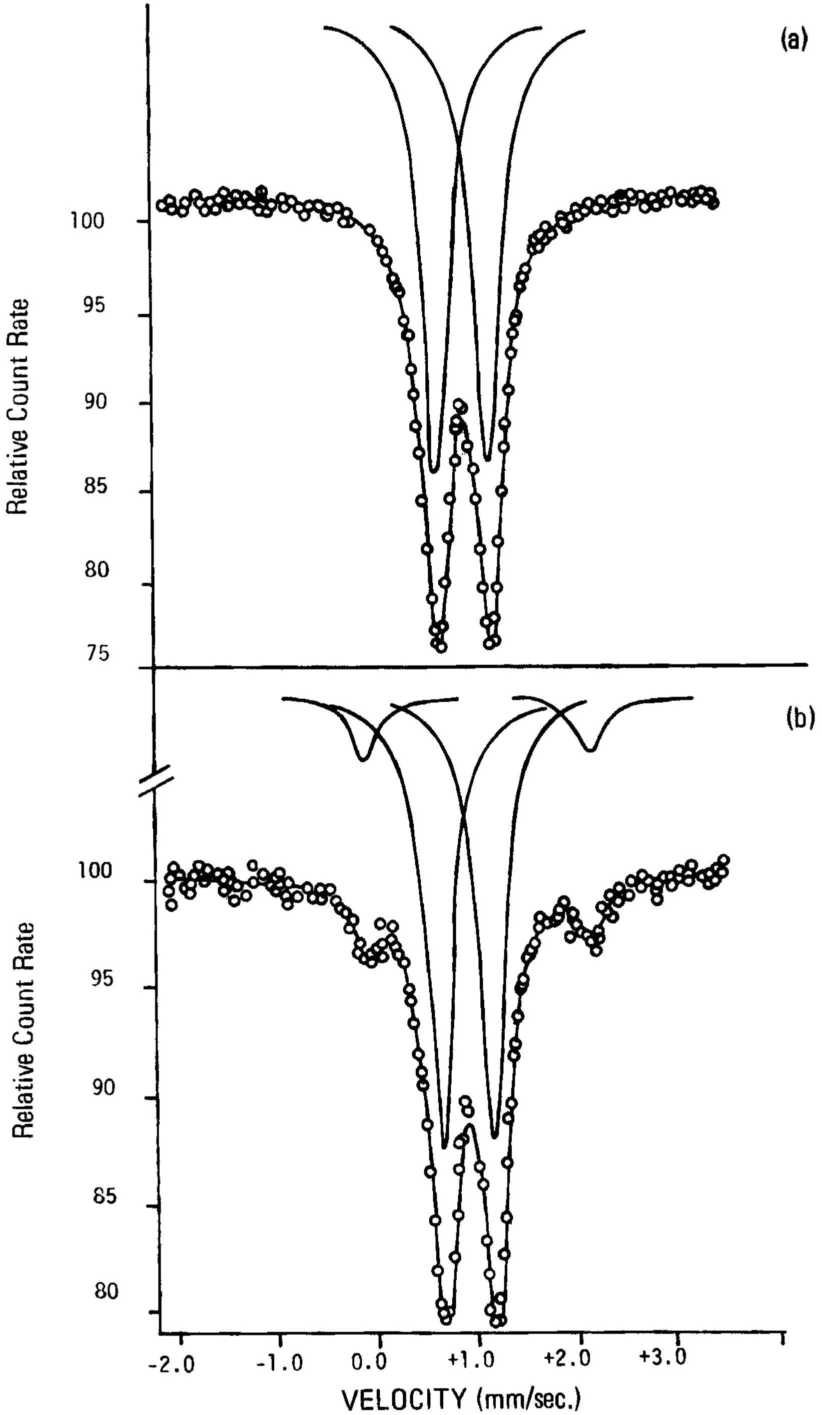


FIG. 4. Mössbauer spectra of (a) Samples 8 and 9—indicative of ferric hydroxy xanthate, (b) Sample 10 (Table 1)—possibly that of ferrous xanthate $Fe(ROCS_2)_2$.

TABLE 2
Mössbauer Parameters for Ferric Ethylxanthate and Related Compounds at 78 °K

Sample no.	Quadrupole splitting, Δ (mm/sec)	Isomer shift, δ (mm/sec)	Line width	
			Γ_1 (mm/sec)	Γ_2 (mm/sec)
1	—	0.728	0.321	—
2	—	0.725	0.330	—
3	—	0.725	0.405	—
4	—	0.727	0.378	—
5	—	0.725	0.323	—
6	0.73	0.71	0.720	0.74
7a	1.09	0.725	0.625	0.53
7b	—	0.730	0.430	—
8	0.58	0.74	0.34	0.35
9	0.58	0.73	0.37	0.36
10a	0.56	0.73	0.31	0.30
10b	2.43	0.86	0.36	0.34

samples, as in Figs. 2, 3, and 4. The circles represent the experimental points; the computed curves are shown as solid lines. The Mössbauer parameters, i.e., the chemical shifts and quadrupole splitting for the samples, as determined from the spectra are given in Table 2. These parameters reflect the interaction of γ-rays with electrons surrounding the nucleus (*8*, *9*). The *chemical shift* enables the oxidation state of the element and the character of bond to be determined, namely for iron

$$Fe^{2+}(3d^6) \rightarrow Fe^{3+}(3d^5)$$

And the *quadrupole splitting*—due to the splitting of energy levels of the excited nucleus in an electric field gradient—gives information about the symmetry of sites in the crystals and the substitution of groups around the central atom.

RESULTS

Figure 2(a) shows the spectrum of Samples 1 to 4, all of which gave identical spectra. The values for isomer shift and line width for all four types of samples given in Table 2 indicate the ferric state of iron ethyl xanthate and are in close agreement with the values obtained by Vainstein et al. (*10*) for their ferric ethylxanthate. All data indicate that ferric ethylxanthate is a low spin compound, with the central iron atom surrounded by six sulfur atoms in octahedral configuration.

Figure 2(b) represents the spectrum of Sample 7, i.e., a 4-week old ferric ethylxanthate precipitated at pH 2.7. The quadrupole splitting and line width values, shown in Table 2 under 7a, do not correspond to any other sample included in this study, and represent an unknown solid, a decomposition product containing Fe^{3+}.

Samples 5 and 6 represent two portions (one was obviously hydrophobic and was floating at the interface of solution/air, the other was sunk to the bottom of the container) of the same precipitate obtained when the final pH of precipitation was 6.2. The floating portion of the precipitate, Sample 5, gave a spectrum identical with that of ferric ethylxanthate, Fig. 2(a). The sink portion, Sample 6, gave a spectrum shown in Fig. 3 and is considered to be due to a ferric xanthate compound in which a substitution by OH group has occurred [i.e., $Fe(OH)X_2$], as indicated by a pronounced quadrupole splitting. Such quadrupole splitting was observed by Wertheim (*8*) in the case of ferrocyanide iron, $K_4Fe(CN)_6 \cdot 3H_2O$, the single line of which becomes resolved into a doublet when one of the CN groups is replaced by a NO group. Similar splitting has been observed for other compounds, e.g., on substitution of a phenyl group by a halide.

An attempt was made to prepare ferrous ethylxanthate by mixing very highly concentrated (1 *M*) solution of ferrous ammonium sulfate with potassium ethylxanthate of similar strength, under different pH conditions. Whenever the final pH was below 3.5, ferric xanthate was formed, as indicated by a spectrum identical to that in Fig. 2(a), as long as the preparation was left open to the atmosphere. However, when the final pH was higher, as for instance, pH 6.2 for Samples 8, 9, or 10, the spectra of samples prepared in partially controlled or entirely open atmosphere were similar [Samples 8 and 9, spectrum Fig. 4(a)] while the sample prepared in carefully controlled inert atmosphere gave a slightly different spectrum shown in Fig. 4(b). Spectra of Samples 8 and 9 are not identical with that of Sample 6, since they differ in the value of quadrupole splitting (see Table 2), but the isomer shift values are indicative of ferric hydroxy xanthate, which may contain a higher proportion of OH group substituted for xanthate groups. The narrowness of lines suggests that a pure chemical compound and not a mixture of closely related materials is involved; it is not a precipitate of ferric hydroxide as this gives two peaks with different isomer shift values. The spectrum in Fig. 4(b) (Sample 10) with a 0.86 mm/sec isomer shift and the quadrupole splitting of 2.43 mm/sec suggests that species of high-spin ferrous xanthate may be present in this sample.

Ferric ethylxanthate (precipitated at pH 3.5 and 25°C) was kept in suspension by magnetic stirring in a solution of pH 9.5 at 45°C for a pro-

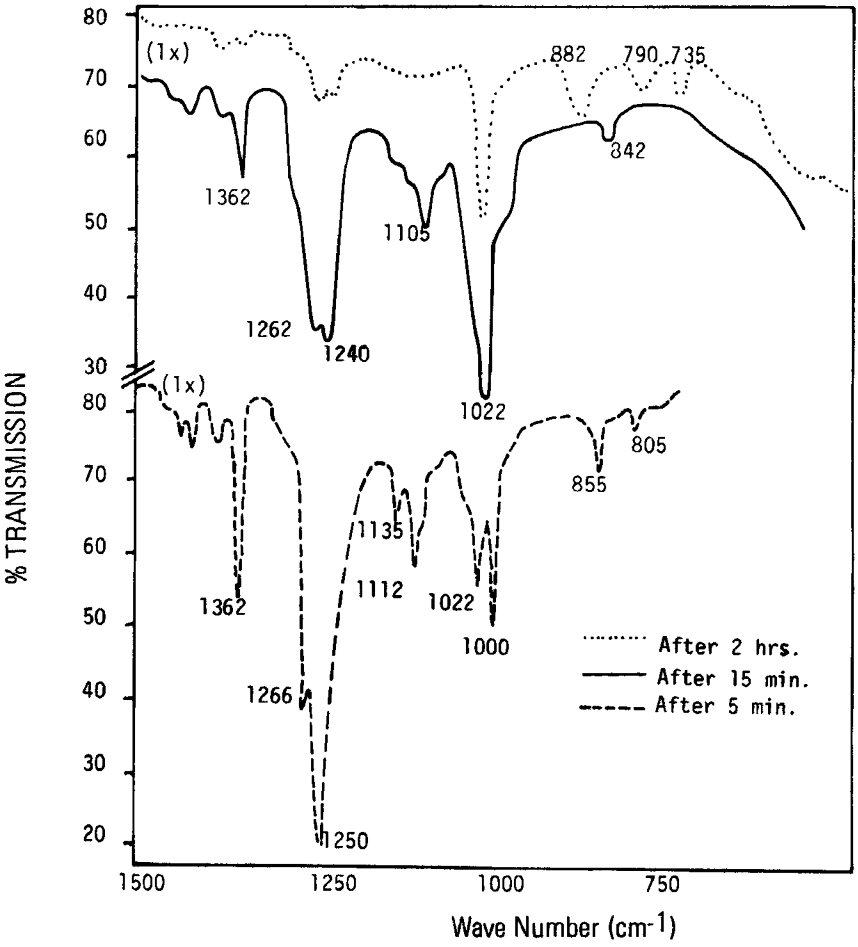


FIG. 5. IR spectra of solids removed from suspension of ferric ethylxanthate at pH 9.5 and 45 °C after the time intervals indicated.

longed period of time and the periodically removed suspended solids were analyzed by IR spectroscopy. The corresponding spectra are given in Fig. 5.

It is seen that after 15 min the spectrum is predominantly that of dixanthogen characterized by the strong 1262, 1240, and 1022 cm^{-1} bands with a 1105 cm^{-1} medium band (*11*). The liquid dixanthogen (at 45°C) was supported on a solid that was identified, by x-ray diffraction, as γ-FeOOH—lepidocrocite. The concentration of dixanthogen was found to decrease with time (after 2 hr) owing to reactions with OH, as independently established by Tipman and Leja (*12*).

CONCLUSIONS

Although the interpretation of the various spectra obtained in this study cannot be unequivocally established without some further work, the results indicate that:

(1) Below pH 3.5, precipitation of iron ions (ferrous or ferric) with ethyl xanthate ion gives the ferric ethylxanthate, characterized by the Mössbauer spectrum shown in Fig. 2(a).
(2) When the pH is higher than 3.5, the ferric xanthate undergoes a change whereby one (or more?) xanthate group is progressively substituted by an OH group; spectra for Samples 6, 8, and 9 are considered similar in character and indicative of a hydroxy complex of ferric xanthate, $Fe(OH)_aX_{3-a}$. Its exact composition cannot be ascertained by Mössbauer spectroscopy.
(3) Ferrous ethylxanthate does not form easily; highly concentrated solutions and neutral or reducing atmosphere must be strictly maintained, otherwise oxidation to the ferric state takes place and leads to the formation of a ferric hydroxy-xanthate complex.
(4) An auxiliary IR study of precipitated ferric xanthate indicated that dixanthogen does form, but as a result of decomposition reactions of the ferric ethylxanthate under alkaline conditions, and not due to a reduction of the ferric to the ferrous ethylxanthate taking place during precipitation.

Acknowledgment

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