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Fundamental Studies on the Collection of Sulphide Minerals with Xanthic Acids. II

Reactions of Formation of Heavy Metal Complexes with Xanthic Acids*

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Synopsis

Spectrophotometric studies were made on the reactions of formation of Pb (II), Ni(II) and Co(II) complexes with ethyl xanthic acid and Co(II) complexes with methyl, n-propyl, n-butyl xanthic acids in acetone-water (1 : 1) solution. The effects of various factors affecting the reactions of formation of these complexes were studied and their compositions and formation constants were evaluated. Xanthic acid reacts with Pb (II), Ni (II) and Co (II) to form only one species of complex, respectively. The composition of Pb(II) complex with ethyl xanthic acid can be represented as 1 : 2, and those of all other complexes as 1 : 3. It may be considered that these complexes form four-membered chelates with two bidentate ligands. The formation constants of PbX_2 and NiX_3^- complexes in acetone-water (1 : 1) solution were determined to be 1.83×10^8 and 0.90×10^{14} , respectively, at 25°C and for an ionic strength of 0.5. The formation constants of Co (II) complexes with methyl, ethyl, n-propyl and n-butyl xanthic acids were determined to be 1.02×10^{12} , 0.98×10^{13} , 3.40×10^{13} and 4.53×10^{13} , respectively. It was found that the logarithmic values of the formation constants of their complexes varied linearly with the values of pKa of xanthic acids. Further it was pointed out that the important relation existed between the effectiveness of xanthic acids as collectors in flotation and the values of the formation constants of their heavy metal complexes.

I. Introduction

Concerning the collecting mechanism of xanthic acids in flotation, considerably large numbers of investigations were carried out previously. Nevertheless a conclusive theory has not been drawn yet. Taggart⁽¹⁾⁻⁽⁴⁾, Wark^{(5),(6)}, and Gaudin⁽⁷⁾⁻⁽⁹⁾ had respectively hypothesized the collecting mechanism from quite

* The 130th report of the Research Institute of Mineral Dressing and Metallurgy. The original report was published in Japanese in Bull. Res. Inst. Min. Dress. Met., **16** (1960) 55.

- (1) T. C. Taylor and A. F. Knoll, Trans. Am. Inst. Mining Met. Engrs. **112** (1934), 382.
- (2) A. F. Taggart, T. C. Taylor, and A. F. Knoll, Trans. Am. Inst. Mining Met. Engrs., **87** (1930), 217.
- (3) A. F. Taggart, T. C. Taylor, and C. R. Ince, Trans. Am. Inst. Mining Met. Engrs., **87** (1930), 285.
- (4) A. F. Taggart, G. R. M. del Giudice, and O. A. Ziehl, Trans. Am. Inst. Mining Met. Engrs., **112** (1934), 348.
- (5) I. W. Wark and A. B. Cox, Trans. Am. Inst. Mining Met. Engrs., **112** (1934), 236.
- (6) I. W. Wark and A. B. Cox, Trans. Am. Inst. Mining Met. Engrs., **134** (1939), 26.
- (7) A. M. Gaudin and R. Schuhmann, Jr., J. Phys. Chem., **40** (1936), 257.
- (8) A. M. Gaudin and G. S. Preller, Am. Inst. Mining Met. Engrs., Tech. Publ. No. 2002 (1946).
- (9) A. M. Gaudin, P. L. deBruyn, and Olav Mellgren, Mining Eng., **8** (1956), 65.

a different point of view. But recently, there is every indication to consider it in connection with the combined action of adsorption and chemical reaction at mineral surface as a cause of hydrophobization. Such conception had been given formerly by Wilkinson et al.⁽¹⁰⁾ and recently was supported by Hagihara^{(11), (12)}, who verified it by means of electron-diffraction method with galena-xanthate system. Sato⁽¹³⁾ applied an electron-diffraction method to sphalerite, activated by copper sulphate, and showed that the formation reaction of copper xanthate is positively dominant against other factors of hydrophobization. Herd⁽¹⁴⁾ and Shimoizaka⁽¹⁵⁾ reported that the hydrophobic film on galena surface is mainly formed by lead xanthate. Hassialis and his associates⁽¹⁶⁾ showed that adsorbed xanthate is movable and moves automatically in the two-dimensional space represented by the interface, and Gaudin⁽¹⁷⁾ pointed out that it would be hard to accept the conclusion of Hassialis et al., if the collector coating were solid and polymolecular, or even a "solid" monomolecular film in the sense in which the term is used by surface chemists. Though it may be supposed that chemical reaction or chemisorption has an important role to the hydrophobization of galena with xanthate, investigators who maintain the chemical reaction theory tried mainly to determine the solubility of heavy metal salts of xanthic acids. Up to the present, studies on the reaction of xanthic acids with heavy metal ions have been disregarded, and no study has been reported on the formation constants of heavy metal complexes with xanthic acids, for instance.

The purpose of the present study is to make clear the formation reactions of heavy metal complexes with xanthic acids and to offer some fundamental data to the collection mechanism of sulphide minerals. For the purpose, a spectrophotometric method was applied to investigate Pb(II), Ni(II) and Co(II) complexes with xanthic acids in acetone-water 1 : 1 solution, and examination was made of various factors affecting the formation reactions, compositions, and formation constants.

In spite of the fact that reactions found in flotation are taking place in water, reactions dealt with in the present study are those in acetone-water 1 : 1 solution, because of the difficulty of resolution of heavy metal xanthate in water. Thus, it would be supposed that it is difficult to apply the present data, as they are, to the analysis of flotation phenomena, but it may be possible to use as fundamental references for collection mechanism of flotation.

Furthermore, they may be expected to be available for the present study when

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(11) H. Hagihara, *J. Phys. Chem.*, **56** (1952), 610.

(12) H. Hagihara, *J. Phys. Chem.*, **56** (1952), 616.

(13) R. Sato, *J. Mining Met. Inst. Japan*, **70** (1955), 63.

(14) H. Herd and W. Ure, *J. Phys. Chem.*, **45** (1941), 93.

(15) J. Shimoizaka, *J. Mining Met. Inst. Japan*, **72** (1957), 11.

(16) M. D. Hassialis and C. G. Myers, *Mining Eng.*, **3** (1951), 961.

(17) A. M. Gaudin, *Flotation*, 2nd ed. (1957), 238.

they are used with Mellor's series^{(18),(19)} and Irving's series⁽²⁰⁾.

II. Experimental apparatus and procedure

In this work, Hitachi EPU-2 photoelectric spectrophotometer with 1 cm path-length quartz cuvette was used for the optical density measurements, and Mitamura DC-II glass electrode pH meter was used for the pH measurements. In exchanging saturated potassium chloride solution in a standard electrode at a fixed time, caution was exercised for the pH measurements of acetone-water solution.

The formation reaction of complexes was performed in the thermostat at $25.0 \pm 0.1^\circ\text{C}$.

Reagents used in all experiments are as follows :

1) Potassium xanthates

Potassium xanthates were prepared by crystallizing samples from acetone solutions, synthesized according to the usual manner in the laboratory. Recrystallization was repeated 3 times by acetone-petroleum ether method. The crystals of pure xanthates were sucked dry and further dried over silica gel, and stored in a dark and cool place. The xanthate solution was prepared whenever experiment was carried out, and stored in a stoppered amber-coloured bottle and rejected when it passed more than 8 hours after preparation.

2) Lead perchlorate, nickel perchlorate and cobalt perchlorate.

Pb(II), Ni(II) and Co(II) were used as perchlorates. The contents of Pb(II) and Ni(II) in solution were determined by a spectrophotometric method using dithizone and dimethylglyoxime⁽²¹⁾, respectively. Co(II) solution was titrated according to the Mayr-Feigl's method⁽²²⁾.

3) Sodium perchlorate

Sodium perchlorate was used to adjust the ionic strength of solutions. This reagent has a strong hygroscopicity, so the determination of concentration was carried out by titrating perchloric acid formed by passing through an ion exchange column of cation exchange resin, Amberlite IR-120H, with sodium hydroxide using phenolphthalein as indicator.

4) Acetone and ethyl alcohol

Acetone, used as solvent, was treated with potassium permanganate and potassium carbonate anhydride, and was distilled at $56.2\text{--}56.3^\circ\text{C}$. In a case of application of iso-sbestic point method to determine the species of complex, ethyl alcohol (b.p. 78.3°C)–water 1 : 1 solution was used as solvent.

In all experiments, pure water, exchanged ionically, was used after distillation.

(18) D. P. Mellor and L. Maley, *Nature*, **159** (1947), 370.

(19) D. P. Mellor and L. Maley, *Nature*, **161** (1948), 436.

(20) H. Irving and R. J. P. Williams, *Nature*, **162** (1948), 746.

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(22) K. Kimura, *Inorganic Quantitative Analysis* (in Japanese), 5 ed., (1956), 359.

III. Experimental results and discussion

1) Reaction of formation of Pb(II) complex with ethyl xanthic acid.⁽²³⁾

a) Effect of the standing time and acidity of solution on the formation of Pb(II) complex with ethyl xanthic acid.

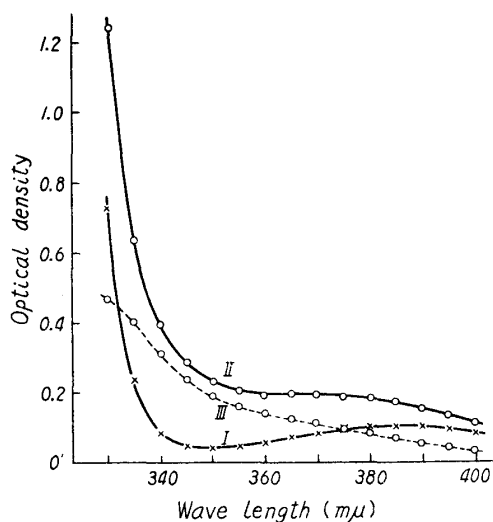


Fig. 1. Absorption spectra of ethyl xanthate and its Pb complex.

I: Solution A— $[\text{C}_2\text{H}_5\text{OCS}_2^-]$ 2×10^{-3} mole/l, acetone-water 1:1, pH 7.0, standing time 1 hr.

II: Solution B— $[\text{C}_2\text{H}_5\text{OCS}_2^-]$ 2×10^{-3} mole/l + $[\text{Pb}^{2+}]$ 18.8 γ /ml, acetone-water 1:1, pH 7.0, standing time 1hr. (reference for I and II: acetone-water 1:1 solution)

III: Solution B (reference: Solution A)

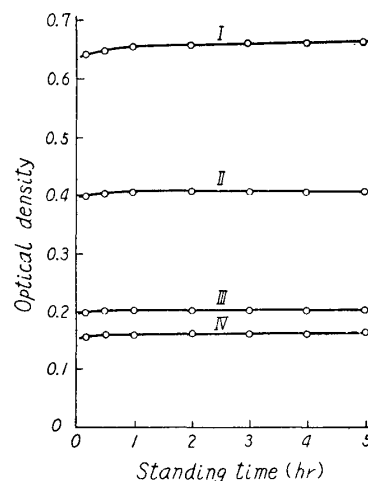


Fig. 2. Effect of the standing time on the formation reaction of Pb complex with ethyl xanthic acid.

$[\text{Pb}^{2+}] = 18.8 \gamma$ /ml, $[\text{C}_2\text{H}_5\text{OCS}_2^-]$ / $[\text{Pb}^{2+}] = 22.0$, pH 7.2.

Wave length: I 335 $m\mu$, II 340 $m\mu$, III 360 $m\mu$, IV 390 $m\mu$.

Absorption spectra of potassium ethyl xanthate and its Pb(II) complex in acetone-water 1:1 solution are shown in Fig. 1. Curve III is the absorption spectra of Pb complex with the reference solution of 2×10^{-3} mole/l of potassium ethyl xanthate. The peak of the absorption band of potassium ethyl xanthate is found at 226 $m\mu$ and 301 $m\mu$.⁽²⁴⁾ Optical density of the absorption peak of Pb complex with ethyl xanthic acid varies with the standing time. As shown in Fig. 2, the optical density reaches a constant value after another hour of standing, which is assumed to complete the reaction of complex-forming. Though the rate of complex-forming reaction is promoted greatly by heat and light, it was not examine to promote the rate of reaction by these methods, because xanthate is very unstable with them.⁽²⁵⁾

Fig. 3 shows that the rate of reaction is controlled with pH. At 30 min. standing, the curve of absorption spectra of pH 9.2 was slightly larger than that

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(25) F. J. Welcher, *Organic Analytical Reagents*, Vol. 4 (1948), 97.

of pH 7.2, but at another hour of standing these absorption spectra showed good agreement. When the hydrogen ion concentration of solution was taken as

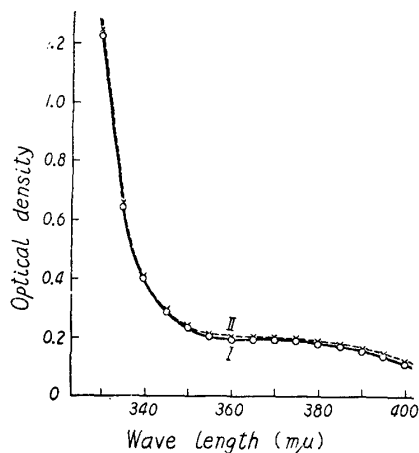


Fig. 3. Effect of pH on the formation reaction of Pb complex with ethyl xanthic acid.
 $[\text{Pb}^{2+}] = 18.8 \gamma/\text{ml}$, $[\text{C}_2\text{H}_5\text{OCS}_2^-]/[\text{Pb}^{2+}] = 22.0$, standing time 30 min, pH: I 7.2, II 9.1

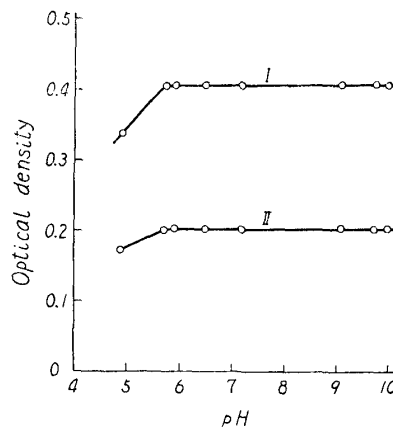
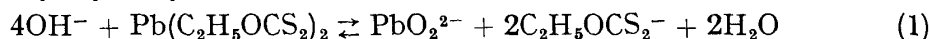


Fig. 4. Effect of pH on the formation reaction of Pb complex with ethyl xanthic acid.
 $[\text{Pb}^{2+}] = 18.8 \gamma/\text{ml}$, $[\text{C}_2\text{H}_5\text{OCS}_2^-]/[\text{Pb}^{2+}] = 22.0$.
 Wave length: I 340m μ , II 360m μ .

parameter, the relationship between the optical density and the pH value was like that illustrated in Fig. 4. The constant value of optical density was obtained in the pH range of 5.7–10.0, but it showed the lower value in the lower pH less than 4.9. Xanthate is unstable in acidified aqueous solution less than pH 5.0^{(1), (26)}, so it may be recognized that the lowering the optical density in the pH lower than 4.9 was mainly due to the decomposition of xanthate. At pH 10.0, the optical density reached a constant value after 10 min. standing, but it began to decrease when the standing time became longer. The absorption spectra of Pb complex at pH 10.0, after the standing time of 15 min. and 1 hr. are shown in Fig. 5. It was observed that the tendency mentioned above was made clear. It may be supposed that this is due to the decomposition reaction of lead ethyl xanthate with hydroxyl ion.

In this connection, Fleming⁽²⁷⁾ showed that lead ethyl xanthate would be decomposed by hydroxyl ion in accordance with



and the speed of reaction depends upon the concentration of hydroxyl ion (at pH 9, about 20 hrs.; and at pH 11, almost immediately).

b) Composition of Pb(II) complex with ethyl xanthic acid.

The composition of Pb(II) complex with ethyl xanthic acid was determined by the continuous variation method^{(28)–(30)}, and result obtained was confirmed by

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(28) Y. Shibata, S. Inoue, and Y. Nakatsuka, J. Chem. Soc. Japan, **42** (1921), 983.

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(30) R. Tsuchida, Bull. Chem. Soc. Japan, **10** (1935), 27.

the chemical analysis of the crystals of lead ethyl xanthate. Fig. 6 shows the

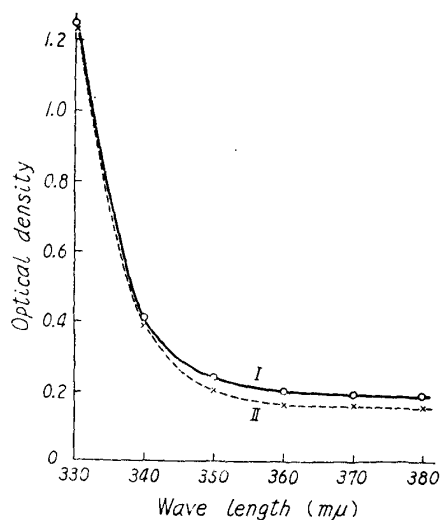


Fig. 5. Absorption spectra of Pb complex with ethyl xanthic acid at pH 10.0.
 $[Pb^{2+}] = 18.8 \gamma/ml$,
 $[C_2H_5OCS_2^-]/[Pb^{2+}] = 22.0$,
 Standing time : I 15 min, II 1hr.

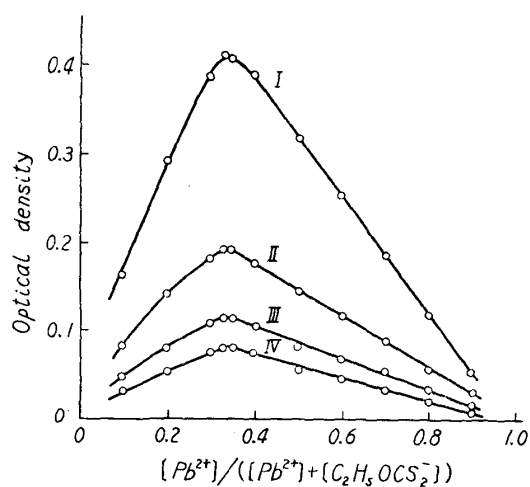


Fig. 6. Composition of Pb complex with ethyl xanthic acid.
 $[Pb^{2+}] + [C_2H_5OCS_2^-] = 3.6 \times 10^{-4}$ mole/l.
 Wave length: I 330 $m\mu$, II 340 $m\mu$, III 350 $m\mu$, IV 360 $m\mu$.

experimental results by the continuous variation method under the condition of

$$[Pb^{2+}] + [C_2H_5OCS_2^-] = 3.6 \times 10^{-4} \text{ mole/l} = \text{const.} \quad (2)$$

As obvious in this figure, the maximum value of the optical density was found when the mixing ratio of $[Pb^{2+}]/([Pb^{2+}] + [C_2H_5OCS_2^-])$ was 0.33. This fact suggests that the only one species of complex having the composition of $Pb^{2+} : C_2H_5OCS_2^- = 1 : 2$ may be formed.

The precipitate, formed by adding a great excess of potassium ethyl xanthate to Pb^{2+} in aqueous solution, was filtered, washed, and dried in vacua, and analysed lead as lead sulphate. The precipitate contained 46.19% Pb. This value is not so different from the theoretical value in the form of $Pb(C_2H_5OCS_2)_2$, 46.10% Pb. The result of this chemical analysis shows the good agreement with that of continuous variation method.

In general it has been well recognized that the coordination number of Pb^{2+} is 4.⁽³¹⁾ Therefore, it may be seen that the composition of lead complex with ethyl xanthic acid obtained in this experiment would be adequately judged from the standpoint of the coordination number of Pb^{2+} . Thus, various structural formulae for Pb complex with ethyl xanthic acid are hitherto presented^{(1), (32)-(34)}, but it may be said that the following formula of four-membered chelates with two

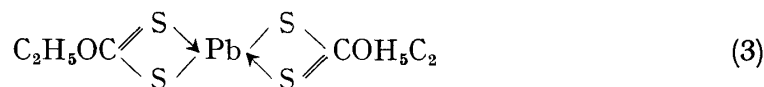
(31) J. C. Bailor, Jr., *The Chemistry of the Coordination Compounds*, (1956), 354.

(32) A. M. Gaudin, F. Dewey, W. E. Duncan, R. A. Johnson, and O. F. Tangel, Jr., *Trans. Am. Inst. Mining Met. Engrs.*, **112** (1934), 319.

(33) G. R. M. del Giudice, *Trans. Am. Inst. Mining Met. Engrs.*, **112** (1934), 398.

(34) A. F. Taggart, *Handbook of Mineral Dressing*, 12-05 (1945).

bidentate ligands would be suitable.



Such a form of four-membered chelate with two bidentate ligands was already given to copper⁽²⁵⁾, palladium⁽³⁵⁾, platinum⁽³⁶⁾, chromium⁽³⁷⁾ compounds. It may be considered from Tsuchida's theory⁽³⁸⁾ that the complex of Pb²⁺ takes the planar structure, and also the same concept was presented by Block⁽³¹⁾. Therefore, it may be said that the same concept can be applied to the case of Pb complex with ethyl xanthic acid, but it is necessary to identify the structure by X-ray method to decide the planar structure.

c) Formation constant of Pb complex with ethyl xanthic acid.

As already reported⁽³⁹⁾, the dissociation constant of ethyl xanthic acid in aqueous solution is 2.9×10^{-2} at 25°C and for an ionic strength of zero. This value become larger with increasing ionic strength. Therefore, in the pH range in which the rate of decomposition of ethyl xanthic ion is considerably slow, for instance in the pH range larger than 5, it may be regarded that ethyl xanthic acid is perfectly dissociated. Hence, the formation reaction of Pb complex with ethyl xanthic acid may progress in accordance with



where X⁻ denotes xanthic ion. The formation constant, K, is

$$K = \frac{[\text{PbX}_2]}{[\text{Pb}^{2+}] [\text{X}^-]^2} \quad (5)$$

To determine the formation constant from the above equation, it is clear that the value of formation constant is influenced greatly by a little error in measuring the concentration, if any one of [PbX₂], [Pb²⁺] and [X⁻] is extremely smaller than the other. Therefore, from the results of preliminary test the quantity of ethyl xanthate added to solution was prepared so as to become 1~1.5 times more than initial concentration of Pb²⁺.

We are well aware of Pb²⁺ precipitates by hydroxyl ion in aqueous solution. For example, it is reported that lead nitrate reacts with ammonium hydroxide and forms lead hydroxide.^{(40), (41)} No reports have been made on the reaction between lead perchlorate and ammonium hydroxide. But if it is assumed that the same reaction as lead nitrate occurs in this case, it cannot precipitate in the pH range lower than 8.5, when the concentration of Pb²⁺ is 1×10^{-4} mole/l, due

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(36) G. Bulmer and F. G. Mann, *J. Chem. Soc.*, (1945), 666.

(37) T. Tsumaki, *Saku-kagobutsu* (Iwanami-koza, Gendai Kagaku, II. D.) (1956), 319.

(38) R. Tsuchida, *Colour and Structure of Metal Compounds* (in Japanese), (1947), 41.

(39) H. Majima, *Bull. Res. Inst. Min. Dress. Met.*, Tohoku Univ., **16** (1960), 41.

(40) J. K. Wood, *J. Chem. Soc.* **97** (1910), 888.

(41) C. A. Jacobson, *Encyclopedia of Chemical Reactions*. Vol. IV (1951), 237.

to the solubility product, 1.1×10^{-5} of lead hydroxide. But in reality, precipitate was formed in the pH range lower than 8.5, as shown in Figs. 7 and 8. These

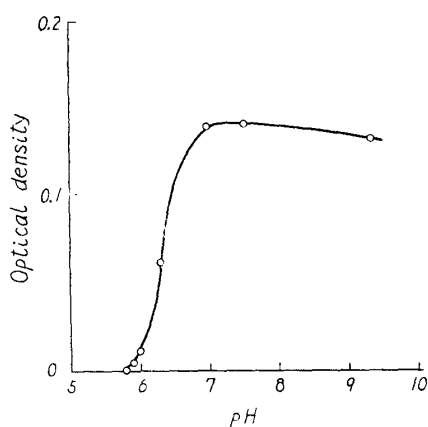


Fig. 7. Reaction between $\text{Pb}(\text{ClO}_4)_2$ and NH_4OH in acetone-water 1 : 1 solution (1).
 $[\text{Pb}^{2+}] = 9.07 \times 10^{-5}$ mole/l, $u = 0.5$, $\lambda = 330 \text{ m}\mu$, standing time 15min.

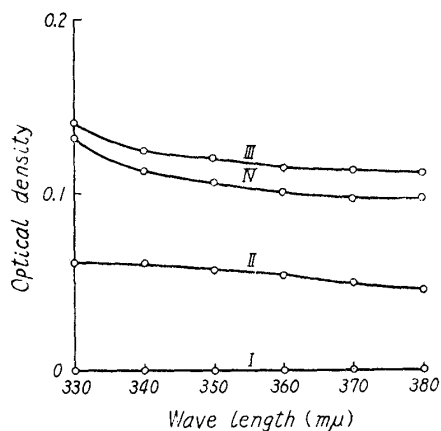


Fig. 8. Reaction between $\text{Pb}(\text{ClO}_4)_2$ and NH_4OH in acetone-water 1 : 1 solution (2).
 $[\text{Pb}^{2+}] = 9.07 \times 10^{-5}$ mole/l, $u = 0.5$, standing time 15 min, pH : I 5.8, II 6.3, III 7.5, IV 9.3.

figures show the formation states of the suspension of lead hydroxide in acetone-water 1 : 1 solution of ionic strength of 0.5. As we see clearly in Fig. 7, percent transmittancy at pH 5.8 is zero, but in the pH range larger than that, it is no longer zero. So in this experiment, the reaction was performed at $\text{pH } 5.74 \pm 0.02$. The formation constant of Pb complex with ethyl xanthic acid at 25°C and for ionic strength of 0.5 was determined, paying attention to the points mentioned above. To estimate the concentration of lead complex with ethyl xanthic acid, the optical density at the wave length of $333 \text{ m}\mu$ was measured intermittently, and its maximum value was introduced for calculation. Reference solution of optical density measurement is the same composition solution except for lead perchlorate. If the measurements were performed in this manner, the optical density, A , should be observed as the difference between the optical density due to lead complex, A_c , and that due to ethyl xanthic ion consumed, A_x . That is, the following equation may be established :

$$A = A_c - A_x = \epsilon_c C_c - n \epsilon_x C_c = C_c (\epsilon_c - n \epsilon_x) \quad (6)$$

where, C_c denotes the concentration of Pb complex with ethyl xanthic acid, ϵ_c , and ϵ_x denote the molar extinction coefficients of Pb complex and ethyl xanthic ion, respectively, and n is the composition of Pb complex. According to Eq. 6, if ϵ_c , ϵ_x , n and A are known, C_c can be estimated. The concentration of ethyl xanthic ion and lead ion in equilibrium condition was estimated by taking off each quantity consumed in complex forming reaction from respective initial concentrations. The molar extinction coefficient of ethyl xanthic ion is 180 at the wave length of $333 \text{ m}\mu$, and that of Pb complex with ethyl xanthic acid is estimated as 4, 574 from the measurement of addition of 120 times ethyl xanthate

in molar concentration over lead perchlorate. Using these value and $n=2$, the concentration of Pb complex was calculated from the actual measured value of optical density.

Table 1 shows the formation constant of Pb complex with ethyl xanthic acid; it was determined to be 1.83×10^8 .

Table 1. Formation constant of Pb (II) complex with ethyl xanthic acid. (25°C, ionic strength 0.5)

Initial conc. of Pb ²⁺ (mole/l)	Initial conc. of C ₂ H ₅ OCS ₂ ⁻ (mole/l)	Optical density (333 mμ) A	Molar extinction coefficient (333mμ)		Conc. of complex (mole/l)	Equilibrium conc. of Pb ²⁺ (mole/l)	Equilibrium conc. of C ₂ H ₅ OCS ₂ ⁻ (mole/l)	Formation constant of complex
			ε _c	ε _x				
9.07 × 10 ⁻⁵	1.12 × 10 ⁻⁴	0.1284	4,574	180	3.047 × 10 ⁻⁵	6.026 × 10 ⁻⁵	5.179 × 10 ⁻⁵	1.89 × 10 ⁻⁸
"	1.20 × "	0.1373	"	"	3.258 × "	5.815 × "	5.482 × "	1.86 × "
"	1.32 × "	0.1500	"	"	3.560 × "	5.513 × "	6.080 × "	1.75 × "
Mean								1.83 × 10 ⁻⁸

2) Reaction of formation of Ni(II) complex with ethyl xanthic acid.

The absorption spectra of potassium ethyl xanthate and its Ni (II) complex in acetone-water 1 : 1 solution of pH 7.3 at 25°C after one-hour standing are shown in Fig. 9. The Curve III in Fig. 9 shows the absorption spectra of Ni(II) complex when acetone-water 1 : 1 solution containing 2 × 10⁻³ mole/l of ethyl xanthate was used as reference solution.

The peak of absorption band of Ni complex was observed at the wave length

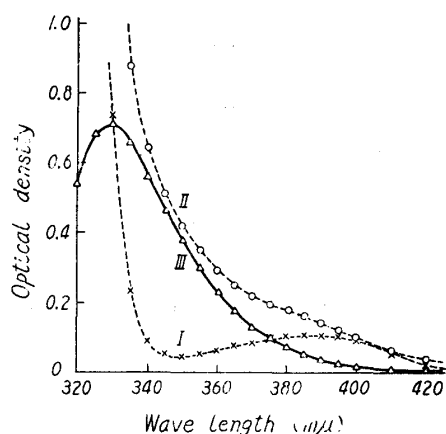


Fig. 9. Absorption spectra of ethyl xanthate and its Ni (II) complex. I : Solution A—[C₂H₅OCS₂⁻] 2 × 10⁻³mole/l, pH 7.3, acetone-water 1 : 1, standing time 1hr. II : Solution B—[C₂H₅OCS₂⁻] 2 × 10⁻³mole/l + [Ni²⁺] 2.96 γ/ml, pH 7.3, acetone-water 1 : 1, standing time 1hr. (reference for I and II : acetone-water 1 : 1 solution) III : Solution B (reference : Solution A)

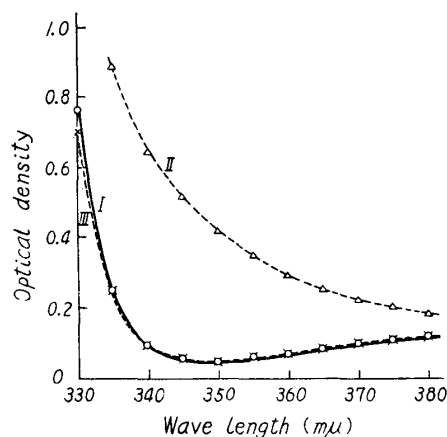


Fig. 10. Absorption spectra of Ni complex with ethyl xanthic acid at pH 12.8. I : [Ni²⁺]=2.96 γ/ml, [C₂H₅OCS₂⁻] / [Ni²⁺]=39.6, acetone-water 1 : 1, pH 12.8. II : ibid, pH 7.3. III : [C₂H₅OCS₂⁻]=2 × 10⁻³mole/l, acetone-water 1 : 1, pH 7.3. (reference for I, II, and III : acetone-water 1 : 1 solution)

of 328 $m\mu$. Besides, at the wave length of 242 $m\mu$ and 600 $m\mu$ the maxima of absorption peak were found. Optical densities at the wave length of 340 $m\mu$ and 350 $m\mu$ increased with the increase of the standing time, and after about 3 hrs. of standing they arrived at their respective constant values. It may be supposed that the arrival of optical density at a constant value means the completion of complex forming reaction. No significant difference was observed between the speed of complex forming reaction at pH 7.3 and that at pH 8.3. And in the pH range of 6.0–9.1, the equilibrium value of optical densities at the wave length of 340 $m\mu$ and 350 $m\mu$ show the respective constant values. But it may be supposed that in a much high range of pH, for example, at pH 12.8, Ni complex once formed is decomposed rapidly.

Fig. 10 shows the absorption spectra of the decomposition products of Ni complex with ethyl xanthic acid at pH 12.8. For the reference, the absorption spectra of ethyl xanthate and its Ni complex at pH 7.3 are shown in the same figure. When the solution of Ni complex was allowed to stand for 30 min. at pH 12.8, the absorption spectra of solution was observed as Curve I shown on Fig. 10. When standing time became longer, no variation in absorption spectra was found. The absorption spectra at pH 12.8 were greatly different from those of Ni complex at 7.3, but they were very similar to those of ethyl xanthate. If it is assumed that one of the decomposition products is ethyl xanthic ion, the suspension of nickel hydroxide should be observed at such pH range. However, the experimental results differ from this assumption. On the other hand, it was observed that the precipitation of nickel hydroxide in acetone-water 1 : 1 solution at pH 12.8 was resolved by adding potassium ethyl xanthate and the absorption spectra of resulting solution agrees with the Curve I in Fig. 10.

From these results it may be supposed that Ni complex with ethyl xanthic acid is decomposed by adding hydroxyl ion, and the decomposition products would not be ethyl xanthic ion and nickel hydroxide.

The composition of Ni complex with ethyl xanthic acid in acetone-water 1 : 1 solution was determined to be 1 : 3 by the continuous variation method. And it is confirmed by the iso-sbestic point method that only one species of complex may be formed in alcohol-water 1 : 1 solution.

Generally, Ni^{2+} forms four- or six-membered compounds, but when it is coordinated with organic ligands, there are many examples in which the six-membered compounds are formed. Hence, the composition determined in this experiment may be regarded as appropriate. Malatesta⁽⁴²⁾ pointed out that only one species of nickel xanthate was formed, and Dubsy⁽⁴³⁾ showed that the composition of nickel xanthate was determined as 1 : 2, but in the present study the composition of Ni complex with ethyl xanthic acid in acetone-water 1 : 1 solution was determined to be 1 : 3.

(42) L. Malatesta, *Gazz. chim. ital.*, **70** (1940), 541.

(43) J. V. Dubsy, *J. prakt. Chem.*, **90** (1914), 90; **93** (1916), 142; **103** (1921), 109.

Formation constant of Ni complex was determined by the method similar to that of Pb complex. The molar extinction coefficient of Ni complex was measured by adding 100 times ethyl xanthate to Ni^{2+} .

Table 2 shows the formation constant of Ni complex with ethyl xanthic acid. It was determined to be 0.90×10^{14} in acetone-water 1 : 1 solution at 25°C and for ionic strength of 0.5.

Table 2. Formation constant of Ni (II) complex with ethyl xanthic acid. (25°C , ionic strength 0.5)

Initial conc. of Ni^{2+} (Mole/l)	Initial conc. of $\text{C}_2\text{H}_5\text{OCS}_2^-$ (mole/l)	Optical density (330m μ) A	Molar extinction coefficient (330 m μ)		Conc. of complex (mole/l)	Equilibrium conc. of Ni^{2+} (mole/l)	Equilibrium conc. of $\text{C}_2\text{H}_5\text{OCS}_2^-$ (mole/l)	Formation constant of complex
			ϵ_c	ϵ_x				
6.732×10^{-5}	1.616×10^{-4}	0.6021	14,592	361	4.457×10^{-5}	2.275×10^{-5}	2.768×10^{-5}	0.91×10^{14}
"	$1.414 \times "$	0.5243	"	"	$3.881 \times "$	$2.851 \times "$	$2.494 \times "$	$0.88 \times "$
"	$1.212 \times "$	0.4437	"	"	$3.284 \times "$	$3.448 \times "$	$2.266 \times "$	$0.82 \times "$
"	$1.010 \times "$	0.3665	"	"	$2.713 \times "$	$4.019 \times "$	$1.959 \times "$	$0.90 \times "$
"	8.078×10^{-5}	0.2882	"	"	$2.133 \times "$	$4.599 \times "$	$1.679 \times "$	$0.98 \times "$
Mean								0.90×10^{14}

3) Reaction of formation of Co(II) complex with ethyl xanthic acid.⁽⁴⁴⁾

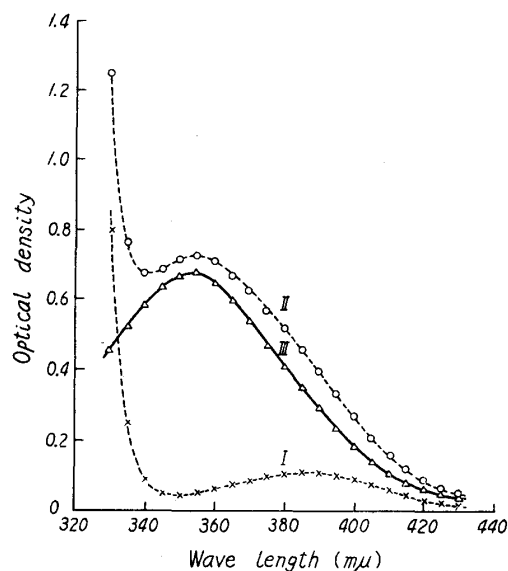


Fig. 11. Absorption spectra of ethyl xanthate and its Co(II) complex.

I: Solution A— $[\text{C}_2\text{H}_5\text{OCS}_2^-] 2 \times 10^{-3}$ mole/l, pH 7.2, acetone-water 1 : 1, standing time 1 hr.

II: Solution B— $[\text{C}_2\text{H}_5\text{OCS}_2^-] 2 \times 10^{-3}$ mole/l + $[\text{Co}^{2+}] 2.56$ $\mu\text{g/ml}$, pH 7.2, acetone-water 1 : 1, standing time 1 hr. (reference for I and II: acetone-water 1:1 solution)

III: Solution B (reference : Solution A)

Fig. 11 shows the absorption spectra of ethyl xanthic ion and its Co(II) complex. The Curve III in Fig. 11 shows the absorption spectra of Co(II) complex with ethyl xanthic acid when acetone-water 1 : 1 solution containing 2×10^{-3} mole/l of ethyl xanthate was used as reference solution. The peak of absorption spectra of Co complex was observed at the wave length of $354 \text{ m}\mu$. The wave lengths of $276 \text{ m}\mu$, $480 \text{ m}\mu$, and $600 \text{ m}\mu$ also show the peaks of absorption band. The optical densities at the wave length of $340 \text{ m}\mu$, $350 \text{ m}\mu$, $360 \text{ m}\mu$ and $380 \text{ m}\mu$ increased with the increase of the standing time, and after about 3 hrs. of standing they reached constant values respectively. It may be seen that the fact mentioned above means the completion of complex forming reaction. The rate of

(44) H. Majima, Suiyokwaishi, **13** (1958), 365.

reaction at pH 9.5 is faster than that at pH 7.2, but the both absorption spectra come to agree with each other as the standing time passes. Optical densities at the wave length of 355 $m\mu$ and 380 $m\mu$ show nearly equal values respectively in the pH range of 5.9–10.2. Though Pb complex with ethyl xanthic acid is decomposed already at pH 10, Co complex is not decomposed at pH 10 even if it is allowed to standing for several hours. But Co complex is decomposed at pH 12.5. It may be supposed that the decomposition of Co complex is led by the same process as that of Pb complex.

The composition of Co complex with ethyl xanthic acid in acetone-water 1 : 1, or alcohol-water 1 : 1 solution was determined by the continuous variation method to be 1 : 3. It is further confirmed from the measurement of iso-sbestic points that only one species of complex may be formed. Co^{2+} formed four- or six-membered compounds, but, in general, it usually form six-membered compounds.^{(31), (45)} Hence, the composition determined in this study may be regarded as appropriate. With regard to this result, Dubsy⁽⁴³⁾ and Kakovskii et al⁽⁴⁶⁾ reported that it is possible to form Co^{3+} salt when the reaction takes place between Co^{2+} and xanthate. It may be considered that Co complex with ethyl xanthic acid formed four-membered chelate with two bidentate ligands and octahedron structure.

The formation constant of Co complex was determined by the method similar to that described in Pb complex. The molar extinction coefficient of Co complex was estimated from the measurement of addition of 184 times as much of ethyl xanthate as Co^{2+} . Table 3 shows the formation constant of Co complex with ethyl xanthic acid, that is, it was determined to be 0.98×10^{13} . This value is recognized to be appropriate, compared with that of Ni complex from the Mellor's series.

Table 3. Formation constant of Co (II) complex with ethyl xanthic acid. (25°C, ionic strength 0.5)

Initial conc. of Co^{2+} (mole/l)	Initial conc. of $C_2H_5OCS_2^-$ (mole/l)	Optical density (354 $m\mu$) A	Molar extinction coefficient (354 $m\mu$)		Conc. of complex (mole/l)	Equilibrium conc. of Co^{2+} (mole/l)	Equilibrium conc. of $C_2H_5OCS_2^-$ (mole/l)	Formation constant of complex
			ϵ_c	ϵ_x				
4.344×10^{-5}	1.043×10^{-4}	0.3307	16,274	28.8	2.043×10^{-5}	2.301×10^{-5}	4.301×10^{-5}	1.12×10^{13}
"	9.122×10^{-5}	0.2692	"	"	$1.663 \times "$	$2.681 \times "$	$4.139 \times "$	$0.87 \times "$
"	$7.820 \times "$	0.2240	"	"	$1.384 \times "$	$2.960 \times "$	$3.668 \times "$	$0.95 \times "$
"	$6.515 \times "$	0.1739	"	"	$1.074 \times "$	$3.270 \times "$	$3.293 \times "$	$0.92 \times "$
"	$5.215 \times "$	0.1302	"	"	$0.804 \times "$	$3.540 \times "$	$2.803 \times "$	$1.04 \times "$
Mean								0.98×10^{13}

4) Reaction of formation of some Co(II) complexes with xanthic acids having

(45) A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, (1952), 152.

(46) I. A. Kakovskii, *Tsvetnye Metally*, **30**, No. 7 (1957), 42; *Battell Tech. Rev.* **6** (1957), 790a.

different carbon numbers of alkyl groups.

The formation reaction of Co(II) complex with ethyl xanthic acid has already been mentioned. It is very interesting to study the effect of different carbon numbers of alkyl groups upon their formation reactions, particularly formation constants. Therefore, the same experiments were carried out with methyl, n-propyl and n-butyl xanthic acids.

The peak of absorption band, 354 m μ , of Co complex with these xanthic acids agrees with that of Co complex with ethyl xanthic acid, but in the molar extinction coefficients are somewhat different from one another.

The experimental results of rate of reaction, composition, and iso-estic point of these complexes are closely similar to those of Co complex with ethyl xanthic acid.

Table 4 shows the formation constants of Co(II) complexes with methyl, n-propyl and n-butyl xanthic acids in acetone-water 1 : 1 solution of pH 7.3 at 25°C and ionic strength of 0.5. The method employed for the determination of formation constant is the same as that described previously.

Table 4. Formation constants of Co (II) complexes with some xanthic acids. (25°C, ionic strength 0.5)

R	Initial conc. of Co ²⁺ (mole/l)	Initial conc. of ROCS ₂ ⁻ (mole/l)	Optical density (354m μ) A	Molar extinction coefficient (354m μ)		Conc. of complex (mole/l)	Equilibrium conc. of Co ²⁺ (mole/l)	Equilibrium conc. of ROCS ₂ ⁻ (mole/l)	Formation constant of complex
				ϵ_c	ϵ_x				
Methyl	4.344×10^{-5}	1.043×10^{-4}	0.1512	13,972	24.0	1.088×10^{-5}	3.256×10^{-5}	7.166×10^{-5}	0.91×10^{12}
	"	9.122×10^{-5}	0.1296	"	"	$0.932 \times "$	$3.412 \times "$	$6.326 \times "$	$1.08 \times "$
	"	$7.820 \times "$	0.0945	"	"	$0.680 \times "$	$3.664 \times "$	$5.780 \times "$	$0.96 \times "$
	"	$6.517 \times "$	0.0726	"	"	$0.522 \times "$	$3.822 \times "$	$4.949 \times "$	$1.13 \times "$
									Mean 1.02×10^{12}
n-Propyl	4.344×10^{-5}	1.043×10^{-4}	0.3893	16,360	26.6	2.391×10^{-5}	1.953×10^{-5}	3.235×10^{-5}	3.54×10^{13}
	"	9.122×10^{-5}	0.3325	"	"	$2.042 \times "$	$2.302 \times "$	$2.996 \times "$	$3.30 \times "$
	"	$7.820 \times "$	0.2782	"	"	$1.709 \times "$	$2.635 \times "$	$2.693 \times "$	$3.32 \times "$
	"	$6.515 \times "$	0.2218	"	"	$1.362 \times "$	$2.982 \times "$	$2.429 \times "$	$3.19 \times "$
	"	$5.215 \times "$	0.1713	"	"	$1.052 \times "$	$3.292 \times "$	$2.059 \times "$	$3.66 \times "$
									Mean 3.40×10^{13}
n-Butyl	4.344×10^{-5}	1.043×10^{-4}	0.4045	16,637	28.4	2.444×10^{-5}	1.900×10^{-5}	3.098×10^{-5}	4.33×10^{13}
	"	9.122×10^{-5}	0.3507	"	"	$2.119 \times "$	$2.225 \times "$	$2.765 \times "$	$4.50 \times "$
	"	$7.820 \times "$	0.2933	"	"	$1.772 \times "$	$2.572 \times "$	$2.504 \times "$	$4.39 \times "$
	"	$6.515 \times "$	0.2373	"	"	$1.434 \times "$	$2.910 \times "$	$2.213 \times "$	$4.55 \times "$
	"	$5.215 \times "$	0.1824	"	"	$1.102 \times "$	$3.242 \times "$	$1.909 \times "$	$4.89 \times "$
									Mean 4.53×10^{13}

When these values were compared with those of Co complex with ethyl xanthic acid, as shown in Table 5, the value of formation constant tended to increase with the increase in the carbon number of alkyl groups. It was recognized that there is a linear relationship between the logarithmic value of stability constant of complex and the pK_a value of complex-forming agent, Cu(II) complex derived from α -amino acid or salicylic aldehyde, and Ag complex with amine may be given

as examples.⁽⁴⁵⁾ It seems that a relationship similar to the above can also be seen in the case of Co(II) complex with xanthic acids. Fig. 12 shows the relationship between the pKa value of xanthic acid⁽³⁹⁾ and the logarithmic value of the formation constant of its Co complex. As obvious in Fig. 12, the pKa value of xanthic acid increase linearly with increasing the logarithmic value of formation constant of its Co complex.

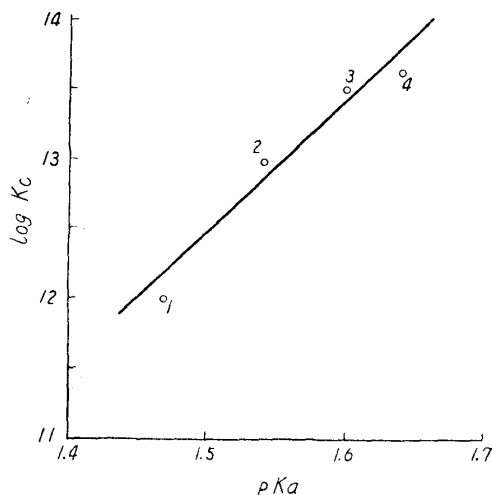


Fig. 12. Relation between the pKa values of dissociation of xanthic acids and the formation constants of their Co(II) complexes.

Species of xanthic acids: 1 methyl-, 2 ethyl-, 3 n-propyl-, 4 n-butyl-.

Table 5. Formation constants of various Co (II) complexes with xanthic acids. (25°C, ionic strength 0.5, acetone-water 1 : 1 solution)

Species of ligands	Formation constants
Methyl xanthic acid	1.02×10^{12}
Ethyl xanthic acid	0.98×10^{13}
n-Propyl xanthic acid	3.40×10^{13}
n-Butyl xanthic acid	4.53×10^{13}

It was found that the collecting power of xanthic acid in flotation is strengthened with the increase in the carbon number of alkyl group.^{(10), (47), (48)} This theory and the experimental results that the quantity of lead xanthate formed on the galena surface will increase with the increase in the carbon number of alkyl group of xanthate, shown by Shimoizaka⁽¹⁵⁾, agree well with the results obtained in the present study.

Summary

Spectrophotometric studies were made of the reactions of formation of Pb(II), Ni(II) and Co(II) complexes with ethyl xanthic acid and Co(II) complexes with

(47) K. L. Sutherland and I. W. Wark, *Principles of Flotation*, (1955), 83.

(48) P. Siedler, *Kolloid-Z.*, **68** (1934), 89.

methyl, n-propyl and n-butyl xanthic acids in acetone-water 1 : 1 solution. The effects of various factors affecting the formation of these complexes were examined and the compositions and formation constants of these complexes were determined.

The results obtained were as follows :

- (1) The complexes dealt with in this study have only one species respectively.
- (2) The composition of Pb (II) complex with ethyl xanthic acid can be represented as 1 : 2, and those of Ni(II) complex and Co(II) complexes with xanthic acids as 1 : 3.
- (3) It is considered that these complexes formed four-membered chelates with two-bidentate ligands.
- (4) The formation constants of PbX_2 and NiX_3^- complexes in acetone-water 1 : 1 solution were determined to be 1.83×10^8 and 0.90×10^{14} respectively at 25°C and for an ionic strength of 0.5. And those of CoX_3^- complexes were determined to be 1.02×10^{12} , 0.98×10^{13} , 3.40×10^{13} and 4.53×10^{13} , respectively, for methyl, ethyl, n-propyl and n-butyl xanthic acids under the same conditions.
- (5) It is well known that the collecting power of xanthic acid in flotation become stronger with the increase in the carbon number of alkyl groups, while the order of magnitude of formation constant obtained for Co(II) complex shows a good agreement with facts mentioned above.
- (6) It was found that the logarithmic values of the formation constants of Co(II) with xanthic acids varied linearly with the values of pK_a of xanthic acids.

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