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Spectrophotometric Studies of Ethyl Xanthate Complexes in Aqueous Solutions

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The stability constants of ethyl xanthate complexes of cadmium(II), zinc(II), nickel(II), and cobalt(II) were determined spectrophotometrically in aqueous solutions. Complexes with the 1 : 1 composition, $M(EX)^+$, were found in all cases; the stability constants of these metal complexes were calculated to be 1.2×10^4, 5.2×10, 4.4×10, and 1.1×10 for $Cd(EX)^+$, $Zn(EX)^+$, $Ni(EX)^+$, and $Co(EX)^+$ respectively at an ionic strength of 1.0 and at 25°C. These values were then compared with the stability constants of other metal complexes.

Potassium or sodium ethyl xanthate (KEX or NaEX) has been employed as a flotation agent for sulfide minerals because it gives hardly soluble metal salts in water. Thus, a large number of investigations have been conducted into the behavior of metal xanthates. However, there has been no report on the complex formation reaction between xanthate and metal ions in aqueous solutions. This may be due to the easy formation of insoluble metal xanthates and to the instability of the xanthate ion (EX^-) in an acidic solution. Majima[1] described the formation of soluble complexes, $Pb(EX)_2$, $Ni(EX)_3{}^-$, and $Co(EX)_3{}^-$, but his work was limited to studies in acetone-water solutions (1 : 1). In our previous paper[2] we have reported on the formation and properties of a tetracoordinate complex, $Cd(EX)_4{}^{2-}$, which was formed by the reaction of the cadmium(II) ion with an excess of EX^- in aqueous solutions.

This investigation was undertaken to examine whether other complexes could be formed by varying the concentration ratios of species of metal ions to EX^-.

The 1 : 1 complexes, $M(EX)^+$ (M: Pb, Cd, Zn, Ni, Co), were found to be formed by 3 methods, the spectrophotometric, kinetic, and solubility methods, in aqueous solutions.

This paper will deal with the spectrophotometric studies; the studies by other methods will be discussed in a subsequent paper.[3]

Experimental

Materials. KEX was prepared according to the usual method and was recrystallized three times from ethyl alcohol and ethyl ether. The product was identified by means of its UV and IR spectra. Perchlorates of cobalt, nickel, and lead were prepared by mixing the metal carbonates with perchloric acid and were then recrystallized twice from water. All the other chemicals were of a guaranteed grade and were used without further purification.

Measurements. A Hitachi recording spectrophotometer, Model EPS-3, and a Shimadzu spectrophotometer, Model QR-50, were used for the measurement of the UV absorption spectra. A Toa Model HM-5A pH meter was used for the pH determination. The

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[1] H. Majima, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **13**, 433 (1961).

[2] T. Yamasaki and M. Nanjo, *Chem. & Ind.*, **1966**, 1530.

[3] M. Nanjo and T. Yamasaki, This Bulletin, **42**, 972 (1969).

ionic strength was adjusted to 1.0 by sodium perchlorate, and both the absorbance and the pH were measured at 25°C. This equilibrium measurement was performed at pH 5—7 in order to avoid the decomposition of EX$^-$.

Results and Discussion

Reaction with the Cadmium(II) Ion. The absorption spectra of a KEX solution recorded in the absence and in the presence of an excess of cadmium(II) ions are presented in Fig. 1. The absorption maxima were found at 226 mμ and 301 mμ. On the addition of cadmium ions a decrease in the absorbance was observed around 301 mμ, but there was no shift in the maximum. A slight blue shift was observed in the band of 226 mμ, and a new weak absorption band appeared in the region between 240 and 260 mμ; the isosbestic points were also observed at 240 and 265 mμ.

The photometric titration curve of a cadmium sulfate solution with a KEX solution at 301 mμ is given in Fig. 2. In Fig. 2, a plateau of absorbance with an intensity of about 70% of the original absorbance of EX$^-$ was obtained. These changes in the absorption spectrum indicate the formation of a complex before the precipitation of bis-(ethylxanthogenato)cadmium(II), Cd(EX)$_2$, starts (K_{sp}: 2.6×10^{-14} or 5.6×10^{-15}).[4,5]

The composition of the complex was determined by employing the continuous variation method[6] in the presence and in the absence of 0.02 M of an acetate buffer solution. In this system, the mole-ratio method is not applicable because of the instability of the complex ion formed. The differences in absorbance, Δd, between the observed values, d, in a 1 cm cell and the values d_0, calculated by assuming that no complex is formed, were plotted against the mole fractions of EX$^-$; the results are shown in Fig. 3. The minimum value of Δd lies at a ratio of 0.5; this indicates the formation of a 1 : 1 complex.

The stability constant of the complex was calculated by using the Rose-Drago method.[7] This

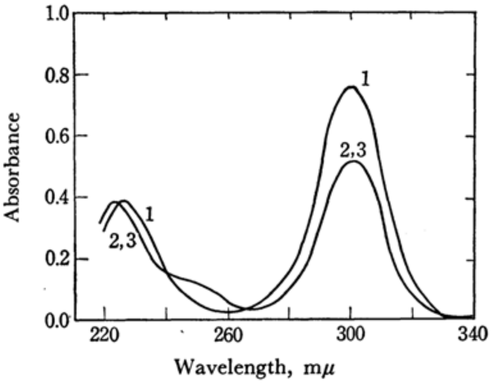

Fig. 1. Absorption spectra of KEX solutions (4.18×10^{-5} M) in the presence of 0.02 M acetate buffer and CdSO$_4$. The contents of CdSO$_4$ are 1) 0, 2) 4.75×10^{-3} and 3) 9.50×10^{-3} M respectively.

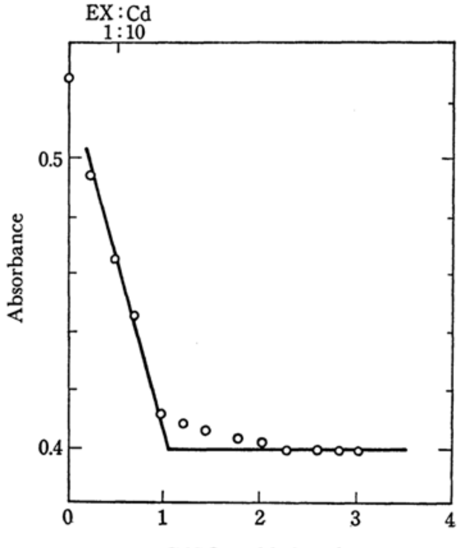

Fig. 2. Photometric titration curve of KEX solution (1.09×10^{-5} M) with CdSO$_4$ (1.02×10^{-2} M) at 301 mμ.

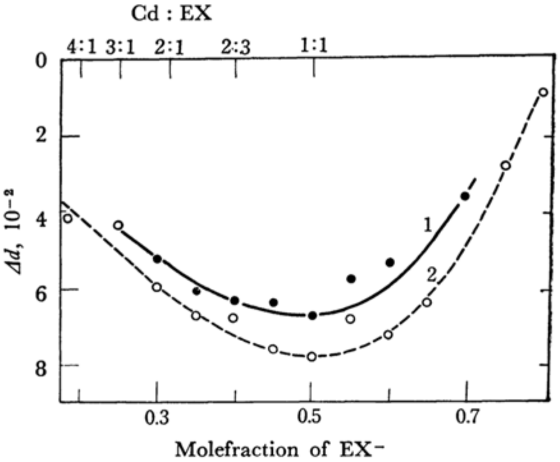

Fig. 3. Continuous variation method. 1) In the absence of acetate buffer, $[\mathrm{EX}^-]_t+[\mathrm{Cd}^{2+}]_t=8.0\times10^{-5}$ M. 2) In the presence of 0.02 M acetate buffer, $[\mathrm{EX}^-]_t+[\mathrm{Cd}^{2+}]_t/1.2=8.0\times10^{-5}$ M, on the assumption of $1+K_{\mathrm{CdOAc}}[\mathrm{OAc}^-]=1.2$.

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[4] A. T. Pilipenko, T. P. Varohenko, E. S. Kudelya and A. P. Kostysina, "Soviet Research on Complex and Coordination Compounds," Part II, p. 1325.

[5] I. A. Kakovsky, "Second International Congress of Surface Activity," Vol. IV, ed. by J. H. Schulman, Butterworth Scientific Publications, London (1957), p. 225.

[6] M. Otomo, This Bulletin, **36**, 137, 889 (1963).

method is applicable when an absorption band of a ligand overlaps with that of a complex, as is shown in Fig. 1. Generally, the equation for the equilibrium is given as follows:

$$M^{2+} + EX^- \overset{K_1}{\rightleftarrows} M(EX)^+. \qquad (1)$$

The concentration equilibrium quotient for this reaction can be written as follows:

$$K_1 = [M(EX)^+]/[M^{2+}][EX^-]. \qquad (2)$$

The absorption of metal ions at a given wavelength was negligibly small compared with that of the complex and EX^-; therefore, the observed absorbance, d, may be expressed as follows:

$$d = \varepsilon_{EX^-}[EX^-] + \varepsilon_{M(EX)^+}[M(EX)^+], \qquad (3)$$

and:

$$d_0 = \varepsilon_{EX^-}[EX^-]_t. \qquad (4)$$

The substitution of $[EX^-]$ and $[M(EX)^+]$ from Eq. (3) into Eq. (2) will give the following equation:

$$K_1^{-1} = (d_0-d)/(\varepsilon_{EX^-}-\varepsilon_{M(EX)^+}) - ([EX^-]_t+[M^{2+}]_t) + (\varepsilon_{EX^-}-\varepsilon_{M(EX)^+})([EX^-]_t[M^{2+}]_t)/(d_0-d). \qquad (5)$$

In Eq. (3) it is assumed that there are at most two absorbing species which obey Beer's law in the concentration range employed. The isosbestic points observed in Fig. 1 show that two absorbing species are present in the solution and that, as Fig. 2 shows, their absorptions obey Beer's law.

The values of K_1 are plotted against $\varepsilon_{Cd(EX)^+}$ in Fig. 4. This procedure is equivalent to solving a simultaneous equation for all possible pairs (K_1 and $\varepsilon_{M(XE)^+}$) of data. The curves show that they intersect at one point and that there is only one complex ion in the solution. From Fig. 4, K_1 was determined to be 1.2×10^4 in the absence of an acetate buffer, and 1.8×10^4 in the presence of a 0.02 M acetate buffer, the formation of the acetatocadmium(II) complex being taken into consideration.[8,9]

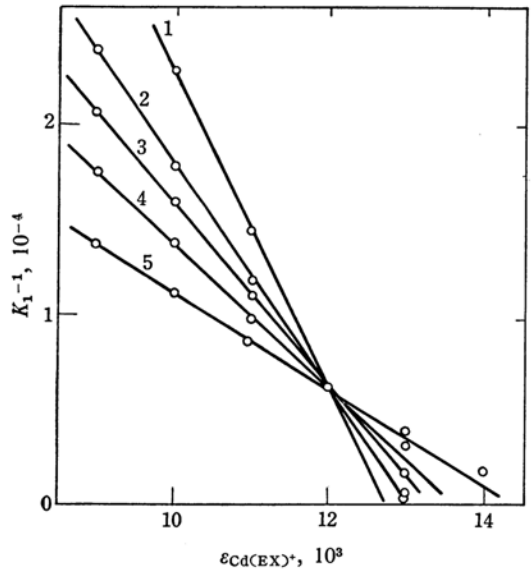

Fig. 4. Rose-Drago's plots at 301 mμ. Each sample solutions contain KEX (3.97×10^{-5} M), 0.02 M acetate buffer and 1) 5.71×10^{-4}, 2) 3.18×10^{-4}, 3) 2.84×10^{-4}, 4) 1.88×10^{-4} and 5) 9.50×10^{-5} M of $CdSO_4$, respectively.

Reaction with Zinc(II) Ions. The experiments were carried out in a 0.2 M acetate buffer solution to prevent the acid decomposition of EX^-. The absorption spectra are shown in Fig. 5. The shapes of the spectra are little different from those of cadmium. The maxima around 301 mμ and 226 mμ show a blue and a red shift respectively, and no new absorption band due to the complex ion could be observed. The isosbestic points were also obtained at 256, 294, and 326 mμ. The absorption of the complex ion obeys Beer's law in an excess of zinc ions. From the Rose-Drago plots, K_1 was determined to be 5.2×10 at 301 mμ, the formation of acetatozinc(II) complex besides the 1 : 1 complex being taken into consideration in a 0.2 M acetate buffer solution.[8] The stability constant employed was 4.6. ($K_{Zn(OAc)^+}$).

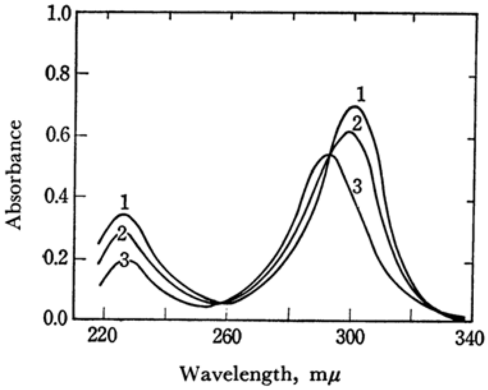

Fig. 5. Absorption spectra of KEX solutions (4.04×10^{-5} M) in the presence of 0.2 M acetate buffer and $Zn(ClO_4)_2$. The contents of $Zn(ClO_4)_2$ in each sample are 1) 0, 2) 4.17×10^{-2} and 3) 1.39×10^{-1} M, respectively.

Reaction with Nickel(II) Ions. The absorption spectra recorded showed a pronounced difference from those of cadmium and zinc, as may be seen in Fig. 6. The isosbestic points were also observed at 285 and 314 mμ, and a new absorption band was obtained around 280 mμ. The absorption band around 301 and 226 mμ showed a red and a blue shift respectively.

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[7] N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

[8] N. Tanaka and K. Kato, This Bulletin, **33**, 417, 1412 (1960).

[9] I. Szilard, Dissertation, ETH, Zürich.

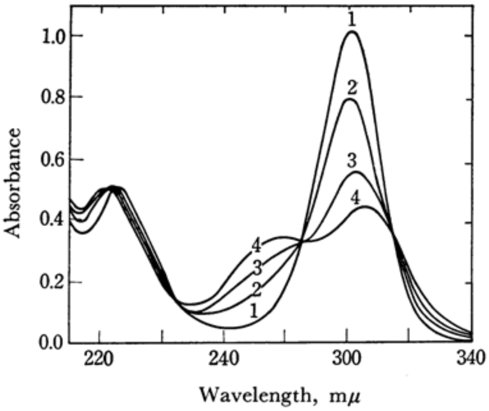

Fig. 6. Absorption spectra of KEX solutions (1.20×10^{-5} M) in the presence of 1) 0, 2) 1.10×10^{-2}, 3) 5.50×10^{-2} and 4) 2.75×10^{-1} M of $Ni(ClO_4)_2$ using 50 mm cells.

Reaction with Cobalt(II) Ions. The sample solution was deairated to protect the cobalt(II) complex from oxidation by air. The absorption spectra are similar in appearance to those of zinc. The band around 301 mμ exhibited a red shift, while the band around 226 mμ showed a blue shift. The isosbestic points were also observed at 240, 288, and 320 mμ, and K_1 was determined to be 1.1×10.

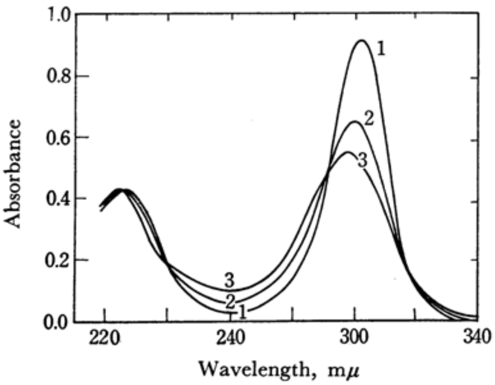

Fig. 7. Absorption spectra of KEX solutions (5.06×10^{-5} M) in the presence of 1) 0, 2) 5.68×10^{-2} and 3) 2.27×10^{-1} M of $Co(ClO_4)_2$ in each sample solutions, respectively.

Reaction with Lead(II), Copper(II), and Magnesium(II) Ions. The dissociation of bis(ethylxanthogenato)lead(II), $Pb(EX)_2$, was so small that all attempts to obtain K_1 by the Rose-Drago method resulted in failure. The absorption spectra observed in an excess of lead(II) ion are presented in Fig. 8. In the case of copper also, the Rose-Drago method could not be employed because of the formation of dixanthogen, $(C_2H_5O\text{-}CSS)_2$, and ethylxanthogenatocopper(I). However in an large excess of copper(II) ions (10^{-3}—10^{-1} M, $[EX^-]_t = 6 \times 10^{-6}$ M), a well-defined absorption spectra was obtained (Fig. 8). The absorption maxima were observed at 258, 283, 327, and 383 mμ, and the band at 283 mμ obeyed Beer's law ($[EX^-]_t$: 3×10^{-6}—3×10^{-5} M). Those absorption bands may be related to the formation of ethylxanthogenatocopper(II) ($Cu(EX)^+$), because the shape of the spectrum differs markedly from that of dixanthogen and the solubility of ethylxanthogenatocopper(I) has been reported to be very low[5] (K_{sp}: 5.2×10^{-23}). A further study by the present authors is in progress; it will be discussed in the near future.

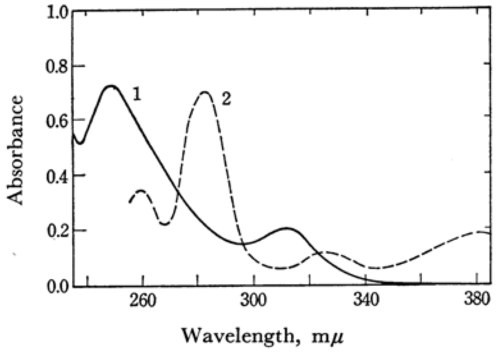

Fig. 8. Absorption spectra of 1) KEX solution (5.0×10^{-5} M) in the presence of 1.34×10^{-3} M of $Pb(ClO_4)_2$ at pH 1.5 and 2) KEX solution (6.55×10^{-6} M) in the presence of 1.24×10^{-1} M of $Cu(ClO_4)_2$ at pH 1.8, using 100 mm cells.

The magnesium(II) ion caused no change in the absorption spectra of EX^-. We failed to prove the formation of any complex by a reaction between magnesium and EX^-.

These results are summarized in Table 1.

TABLE 1. STABILITY CONSTANTS OF 1 : 1 COMPLEXES 25°C, $\mu = 1$ ($NaClO_4$)

Metal ion	K_1
Cd(II)	$(1.2 \pm 0.1) \times 10^4$ $(1.8 \pm 0.2) \times 10^4$ [a]
Zn(II)	$(5.2 \pm 0.1) \times 10$ [b]
Ni(II)	$(4.4 \pm 0.3) \times 10$
Co(II)	$(1.1 \pm 0.1) \times 10$
Mg(II)	no complex formed

a) In the presence of 0.02 M acetate buffer.
b) In the presence of 0.2 M acetate buffer.

From the kinetic data,[3] the value of K_1 for $Pb(EX)^+$ was determined to be $(2.5 \pm 0.4) \times 10^4$. The order of K_1 decreases in the series as follows:

$$Pb > Cd \gg Zn > Ni > Co > Mg\,.$$

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[10] D. P. Mellor and L. Maley, *Nature,* **159**, 370 (1947).

The Mellow-Maley series,[10] Mg<Mn<Fe<Cd<Zn<Co<Pb<Ni<Cu<Pd, which holds for oxygen and nitrogen ligands, is a direct consequence of their ionization potentials and ionic radii. In the case of Cr(II) and Cu(II), a factor of Jahn-Teller is added to them.

On the other hand, cadmium(II) and lead(II) behave differently toward sulfur of a soft-base compound like EX$^-$, but they do not belong to the first raw transition series. For these two metal ions the possibility of some degree of L→M π-bonding in the complexes has been pointed out by Irving and Fernelius.[11]

It appears probable that lead(II) and cadmium(II) complexes are stabilized by the π-bonding and do not obey the Mellor-Maley series, because this series was proposed without taking the π-bonding into consideration.

The absorption spectra of EX$^-$ in the presence of an excess of cadmium(II) and lead(II) ions showed a band around 250 mμ which could not be observed in the case of other metals. The absorbance of the ethylxanthogenatolead(II) ion around 250 mμ is stronger than that of cadmium. From these observations and the fact that the stability of the lead complex is highest, the new absorption band around 250 mμ may be explained as a reflection of the L→M π-bonding.

The question whether these absorption bands arose from n-π^* or π-π^* transition in the complexes was not resolved by these studies, but the studies to explain the shift of the absorption bands of EX$^-$ due to the complex formation are in progress by the authors from the view-point of the metal-sulfur bond character, as has been proposed by Pearson.[12]

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11) R. J. Irving and W. C. Fernelius, *J. Phys. Chem.*, **60**, 1427 (1956).

12) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).