CHLOROFORM EXTRACTION OF CADMIUM AND ZINC WITH METHYL, ETHYL,
PROPYL, AND BUTYL XANTHATES

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The extraction behavior of cadmium and zinc with methyl, ethyl, propyl, and butyl xanthates into chloroform was studied spectrophotometrically. It was found that the extracted species were the type of $M(\text{xanthate})_2$ in all cases. In addition, the overall formation constants and the distribution constants for these complexes were determined. In the systems of methyl and ethyl xanthates, the water-soluble complexes having a formula of $M(\text{xanthate})_3^-$ were formed in the presence of a large excess of xanthate. The stability of $M(\text{xanthate})_2$ increased in the order methyl < ethyl < propyl < butyl xanthate, and a linear free energy relationship was observed between the basicity (pK_a) of xanthate and the stability ($\log \beta_2$) of complex.

INTRODUCTION

Alkyl xanthates (*O*-alkyl dithiocarbonates, abbreviated as X) react with many metal ions to give chelates which are sparingly soluble in water but readily soluble in organic solvents such as chloroform¹⁾. This property of xanthates is of interest in separation analysis. Ethyl xanthate has especially been used as a reagent for the solvent extraction of metal ions²⁾. However, there are few thermodynamical investigations on the solvent extraction since xanthates are unstable in acid media.

The author and co-workers have studied the solvent extraction of several metal-xanthate complexes, and reported the compositions and the formation constants of the extracted complexes³⁻⁷⁾. In addition, it was confirmed that water-soluble complexes such as MX_3^- or MX_4^{2-} were formed in the presence of a large excess of xanthate in the systems of cadmium and zinc benzyl(BeX) xanthates⁵⁾ and zinc ethyl xanthate³⁾.

This paper describes the composition of the extracted species and the formation and distribution constants of the complexes formed in the chloroform extraction of cadmium and zinc with methyl(MeX), ethyl(EtX), propyl(PrX), and butyl(BuX) xanthates.

EXPERIMENTAL

Reagents

Potassium salts of the alkyl xanthates were synthesized according essentially to the method of Price et al.⁸⁾ with corresponding alcohols, carbon disulfide, and potassium hydroxide. These salts were recrystallized three times from solutions of the corresponding alkyl alcohols, washed with ethyl ether, dried in vacuo, and stored in a refrigerator. All xanthate solutions were freshly prepared daily.

Stock solutions of cadmium and zinc were prepared by dissolving cadmium nitrate tetrahydrate and zinc nitrate hexahydrate in 0.1 mol dm^{-3} nitric acid, respectively. These solutions were standardized volumetrically with EDTA (Cd^{2+} : $1.986 \times 10^{-2} \text{ mol dm}^{-3}$; Zn^{2+} : $1.036 \times 10^{-2} \text{ mol dm}^{-3}$).

Apparatus

A Shimadzu Model UV-200 spectrophotometer with 1 cm quartz cells and a Toa Model HM-9A pH meter with a glass electrode were used for spectrophotometric and pH measurements, respectively. A thermostat equipped with a Taiyo thermo unit "Minder Junior" was used to maintain the temperature of the solution at $25 \pm 0.5^\circ \text{C}$ during the extraction period.

Procedure

All solutions were previously thermostated at 25°C . The solution of cadmium or zinc was taken into a 50 cm^3 measuring cylinder equipped with a Teflon stopper. An ionic strength of the solution was adjusted to 1.0 with potassium nitrate and desired pH values were obtained by the addition of potassium hydroxide solution. A proper amount of potassium xanthate solution was added, and the total volume of the solution was made up to 20.0 cm^3 with water. After the addition of 15.0 cm^3 of chloroform, the cylinder was shaken vigorously for 1 min and allowed to stand in the thermostat for 4 min. The shaking and standing was further repeated 3 times to ascertain complete equilibration. The chloroform phase was separated and dried with anhydrous sodium sulfate. The absorbance of the organic phase was then measured against the reagent blank at a fixed wavelength. The pH of the aqueous phase was also measured.

RESULTS AND DISCUSSION

Effect of pH on extraction

The complexes extracted into the chloroform phase gave the absorption spectra having an absorption maximum in the ultraviolet region, the absorption maxima of the cadmium complexes of MeX, EtX, PrX, and BuX being found at 305, 306, 307, and 305.5 nm, respectively. Similarly, those of the zinc complexes of MeX, PrX, and BuX were found at 301.5, 300, and 301.5 nm, respectively.

The degree of the extraction of these metals was determined on the basis of the absorbance of the chloroform phase at each maximum wavelength. The relationships between the absorbance of chloroform phase and the final pH of aqueous phase were shown in Figs. 1 (for cadmium) and 2 (for zinc). A plateau was observed in each system except the zinc-MeX system. The decrease in absorbance on both sides of the plateau may be due to the acid decomposition of the xanthates in the lower pH region and the hydrolysis of metal ions in the higher pH region. The optimum

Fig. 1. Effect of pH on extraction of cadmium.

V_{aq} : 20 cm^3 ; V_{org} : 15 cm^3 ; $[\text{Cd}^{2+}]$: 4×10^{-5} (for I), $2 \times 10^{-5} \text{ mol dm}^{-3}$ (for II, III, & IV); [xanthate]: 5×10^{-3} (for I), $2 \times 10^{-3} \text{ mol dm}^{-3}$ (for II, III, & IV).

Fig. 2. Effect of pH on extraction of zinc.

V_{aq} : 20 cm^3 ; V_{org} : 15 cm^3 ; $[\text{Zn}^{2+}]$: $2 \times 10^{-5} \text{ mol dm}^{-3}$; [xanthate]: 1×10^{-2} (for I), 5×10^{-3} (for II), $2 \times 10^{-3} \text{ mol dm}^{-3}$ (for III).

pH range for the extraction of cadmium and zinc increased in the order $\text{MeX} < \text{EtX} < \text{PrX} < \text{BuX}$. This indicates that the extractability of complex increases in the same order.

Effect of concentration of xanthate on distribution ratio of metal

The effect of the concentration of xanthate on the absorbance of the organic phase was investigated under the condition of the optimum pH for each system. The zinc-MeX system with no plateau pH region was not examined.

The molar absorptivity (ϵ) for each complex in chloroform at the maximum wavelength was calculated from a sum of the absorbances for the first and the second extracts.

The distribution ratio (D) of metal can be calculated from the following equation:

$$D = \frac{\frac{A}{\epsilon}}{C_M - \frac{A}{\epsilon} \times \frac{V_{org}}{V_{aq}}} \quad (1)$$

Where, C_M is the total concentration of metal, A is the absorbance measured, while, V_{org} and V_{aq} are the volumes of organic and aqueous phases, respectively.

Figures 3 and 4 show the relationships between the concentration of xanthate and the distribution ratio of cadmium and zinc.

Fig. 3. Relation between distribution ratio of cadmium and concentration of xanthate ion.

I: MeX; II: EtX;
III: BeX(cited from Ref. 5);
IV: PrX; V: BuX.

Fig. 4. Relation between distribution ratio of zinc and concentration of xanthate ion.

I: EtX(cited from Ref. 5);
II: BeX(cited from Ref. 5);
III: PrX; IV: BuX.

In these figures, the numerical values on the abscissa indicate the concentration of free xanthate ion in the aqueous phase at the extraction equilibrium, and this concentration is estimated as follows:

- 1) It is considered that potassium xanthate in aqueous solution is perfectly dissociated into ions, because the pH of the solution under the experimental conditions is in the range of 7.5 - 8.5 and the acid dissociation constants (pK_a) of the xanthates used are less than 2.
- 2) Xanthates are unstable in an acidic aqueous solution and decompose into carbon disulfide and the original alcohols. The rate of the decomposition depends seriously on the acidity of solution but very slow above pH 7. For this reason, the decomposition of xanthate during the experiment can be neglected.
- 3) The quantity of free xanthate extracted into the chloroform phase can be ignored in comparison with that of free xanthate ion in the aqueous phase.
- 4) The extracted species is assumed to be only MX_2 .
- 5) On the basis of these considerations, the free xanthate ion concentration in the aqueous phase at the extraction equilibrium can be expressed by the following equation:

$$\begin{aligned}
 [X^-]_{eq} &= C_X - 2[MX_2]_{org} \times \frac{V_{org}}{V_{aq}} - 2[MX_2]_{aq} \\
 &= C_X - 2\left(\frac{V_{org}}{V_{aq}} + \frac{1}{K_p}\right) \frac{A}{\epsilon}
 \end{aligned} \quad (2)$$

Where, C_X is the total concentration of xanthate and K_p the distribution constant of MX_2 .

Formation constant and distribution constant

When it is assumed that the complexes formed in aqueous solution are MX^+ , MX_2 , and MX_{2+m}^{m-} and that the extractable species is only MX_2 , the distribution ratio of metal is represented by the following equation:

$$D = \frac{[MX_2]_{org}}{[M^{2+}]_{aq} + [MX^+]_{aq} + [MX_2]_{aq} + [MX_{2+m}^{m-}]_{aq}} \quad (3)$$

Equation (3) is transformed into eqn. (4) by the use of the formation constants (β_n) and the distribution constant.

$$D = K_p \left(\frac{1}{\beta_2 [X^-]^2} + \frac{\beta_1}{\beta_2 [X^-]} + 1 + \frac{\beta_{2+m}}{\beta_2} [X^-]^m \right)^{-1} \quad (4)$$

If the concentration of xanthate is sufficiently low, eqn. (4) can be simplified to eqn. (5).

$$\log D = \log K_p + \log \beta_2 + 2 \log [X^-] \quad (5)$$

Equation (5) shows that a plot of $\log D$ vs. $\log [X^-]$ gives a straight line with a slope of 2. The same relationships held in all extraction systems examined, as shown in Figs. 3 and 4. The assumption of MX_2 to be extracted was amply justified by these results.

If the concentration of xanthate is high enough, eqn. (4) can also be simplified to eqn. (6).

$$\log D = \log K_p + \log (\beta_2 / \beta_{2+m}) - m \log [X^-] \quad (6)$$

Equation (6) shows that the linear relationship having a slope of minus m exists between $\log D$ and $\log [X^-]$. This relationship was only observed in the systems of cadmium-MeX and cadmium-EtX. In these systems the value of m was unity, and then the formation of $Cd(MeX)_3^-$ and $Cd(EtX)_3^-$ was indicated. In the other systems in which no complex of the MX_{2+m}^{m-} type was formed, it was expected that the distribution ratio was nearly equal to the distribution constant being independent on the concentration of xanthate, as shown in Figs. 3 and 4.

The formation constants and the distribution constants for each system could be determined from the plots of Figs. 3 and 4 by the use of eqn. (4). However, the value of β_1 except for the system of zinc-PrX, could not be obtained because it was significantly smaller than that of β_2 . The solid lines in Figs. 3 and 4 are the theoretical curves calculated on the basis of eqn. (4) in which the constants are obtained by the above-mentioned method. The observed values were in

Table 1. Properties of cadmium- and zinc-xanthate complexes.

		MeX	EtX	BeX	PrX	BuX
Cd	$\log \beta_2$	7.0 ₀	7.9 ₂	8.5 ₈ ^a	9.2 ₀	10.2 ₅
	$\log \beta_3$	9.4 ₈	10.3 ₄	—	—	—
	$\log \beta_4$	—	—	15.1 ^a	—	—
	$\log K_p$	0.9 ₂	1.7 ₈	1.9 ₂ ^a	1.5 ₅	1.2 ₅
	$\frac{\lambda_{\max} \text{ of } MX_2}{\text{nm}}$	305	306	—	307	305.5
	$\frac{\epsilon \text{ at } \lambda_{\max}}{10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3}$	1.76	1.78	—	1.93	1.85
Zn	$\log \beta_1$	—	—	—	3.2 ₄	—
	$\log \beta_2$	—	4.3 ₂ ^b	5.3 ₅ ^a	6.3 ₀	6.8 ₆
	$\log \beta_3$	—	5.3 ₀ ^b	7.4 ₉ ^a	—	—
	$\log K_p$	—	1.4 ₈ ^b	2.5 ₅ ^a	1.1 ₅	1.8 ₀
	$\frac{\lambda_{\max} \text{ of } MX_2}{\text{nm}}$	301.5	300 ^b	—	300	301.5
	$\frac{\epsilon \text{ at } \lambda_{\max}}{10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3}$	—	2.03 ^b	—	2.31	1.97
pK_a		1.4 ₁ ^c	1.4 ₆ ^c	1.5 ₀ ^d	1.5 ₁ ^c	1.5 ₈ ^c

a: cited from Ref. 5 ;

b: cited from Ref. 3 ;

c: cited from Ref. 9 ;

d: cited from Ref. 10.

good agreement with theoretical ones. Therefore, these constants were valid. The results are summarized in Table 1 together with those reported on other systems.

A linear free energy relationship¹¹⁾ was observed between the stability of complex and the basicity of xanthate, that is, each plot of $\log \beta_2$ vs. pK_a for the cadmium and the zinc systems gave a straight line as well as for the systems of BeX. These lines were parallel each other and the complex of cadmium was always more stable than the corresponding zinc complex. The difference in logarithmic value of β_2 is about 3.3. As cadmium ion is more "soft" as Lewis acids than zinc ion, the former should give more stable complex with xanthate which coordinates through two sulfur atoms.

The formation of MX_{2+m}^{m-} becomes more difficult with increasing carbon number of the alkyl group in the xanthate molecule. It may be due to the structural factors and the increase in the stability of MX_2 .

In general, it is difficult to separate cadmium or zinc from their mixtures because these metals are members of the same group in the periodic table. The results obtained, however, suggest the possibility of mutual separation of these

metals by solvent extraction. Namely, it seems that cadmium should be extractively separated from zinc with 10^{-4} - 10^{-3} mol dm $^{-3}$ EtX in the presence of an appropriate masking agent such as ammonia as one of "hard bases". Zinc should also be extracted into chloroform and separated from cadmium by using 10^{-2} - 10^{-1} mol dm $^{-3}$ BeX as the extractant.

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