Acid Dissociation Constants of Alkyl Xanthic Acids and Formation Constants of Cadmium(II) and Zinc(II) Xanthato Complexes in 1:1 v/v H_2O-DMF Medium

Kenjiro HAYASHI,* Yoshiaki SASAKI, Shigehiro INOMATA, and Takagimi YANAGIDANI
Department of Chemistry, Faculty of Science, Yamaguchi University,
Yoshida, Yamaguchi-shi 753

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The overall formation constants, β_3, of cadmium(II) and zinc(II) complexes with alkyl xanthates (*O*-alkyl dithiocarbonates) were determined by polarography in the 1:1 v/v water-*N*,*N*-dimethylformamide mixture. The values of these constants increase in the order, methyl<ethyl<propyl<butyl<2-methylpropyl<1-methylethyl xanthate. This order agrees entirely with the order of the basicity of alkyl xanthates determined by using the kinetic parameter of the acid decomposition of xanthates.

Alkyl xanthates (*O*-alkyl dithiocarbonates, $ROC(S)S^-$, abbreviated as X^-) have been used as chelating reagents for the solvent extraction of metal ion.[1] However, the thermodynamical property of the metal xanthato complexes has not yet become clear sufficiently.

The present authors have studied the solvent extraction of several metal xanthato complexes, and reported the compositions and the formation constants of the extracted complexes.[2–5] Furthermore, the water-soluble complexes having a formula MX_3^- or MX_4^{2-} ($M=Cd^{2+}$, Zn^{2+}) were found to be formed only with methyl and ethyl xanthates in the presence of a large excess of xanthate[6,10].

All the cadmium(II) and zinc(II) xanthato complexes formed in the water-*N*,*N*-dimethylformamide(DMF) mixture were soluble in this mixture. Therefore, the compositions and the stability constants of these soluble complexes were determined by polarography. The apparent acid dissociation constants of alkyl xanthic acids (*O*-alkyl dithiocarbonic acids, HX) in the same medium were also determined, and the effect of the basicity of the ligand on the stability of the complex was studied.

Experimental

Reagents. Potassium salts of alkyl xanthates were synthesized from corresponding alkanols, carbon disulfide, and potassium hydroxide as described previously.[6] The solutions of xanthates were prepared immediately before use.

The stock solutions (0.02 mol dm^{-3}) of cadmium(II) and zinc(II) were prepared by dissolving each nitrate salt in 0.1 mol dm^{-3} nitric acid. These solutions were standardized volumetrically with EDTA.

Apparatus and Procedures. (1) The decomposition rate of xanthate in the 1:1 v/v water-DMF medium was measured spectrophotometrically at 305 nm which is an absorption maximum wavelength of xanthate on a Hitachi Model 139 spectrophotometer (for moderate decomposition) and a Union Giken Model RA-401 stopped-flow spectrophotometer (for fast decomposition). Each cell chamber was thermostated at 25 °C with a water jacket. The ionic strength of test solutions was kept at 0.4 mol dm^{-3} with potassium chloride (the use of nitrate salt was unfavorable because of the absorption of light in ultraviolet region and the oxidation of the xanthates in an acid solution). The pH of the solutions was controlled by using the potassium acetate-hydrochloric acid buffer solution.

(2) Direct current polarographic waves were recorded with a Yanaco Model P8 polarograph using a three-electrodes format with mercury as an auxiliary electrode and saturated calomel electrode as a reference electrode. The dropping mercury electrode used had an m value of 1.18 mg s^{-1} and a drop time of 5.67 s at open circuit at a height of mercury reservoir of 69.0 cm. All polarographic measurements were made in the 1:1 v/v water-DMF medium containing 5×10^{-4} mol dm^{-3} metal ion, proper amount of xanthate, and 0.002% Triton X-100 as a maximum suppressor at 25.0±0.2 °C under the air-free condition. The ionic strength of the test solutions was made 0.4 mol dm^{-3} by the addition of potassium nitrate, and pH was adjusted with nitric acid or potassium hydroxide solution.

Results and Discussion

(1) Acid Dissociation Constant of Xanthic Acid. Alkyl xanthates are quite unstable in an acid solution and decompose. The dissociation constant of xanthic acid in the water-DMF mixture system was determined according to the method of Iwasaki and Cooke,[7] who determined the constant in an aqueous medium.

The decomposition rate equation introduced by them is as follows:

$$-\frac{\mathrm{d}\ln([X^-]+[HX])}{\mathrm{d}t}=\frac{k_3}{1+K_a[H^+]^{-1}}\equiv\kappa \tag{1}$$

or

$$\log\frac{(\text{Absorbance})_1}{(\text{Absorbance})_2}=\frac{\kappa}{2.303}(t_2-t_1), \tag{2}$$

where k_3 and K_a are the decomposition rate and dissociation constants of xanthic acid, and $(\text{Absorbance})_1$ and $(\text{Absorbance})_2$ denote the absorbances at time t_1 and t_2, respectively.

A linear relationship of Eq. (2) held between the time elapsed after the preparation of xanthate solution and the absorbance at 305 nm. It is satisfactory to consider that Eq. (2) is valid not only in an aqueous medium but also in the 1:1 v/v water-DMF mixture.

The log-values of κ were calculated on the basis of the slopes of plots according to Eq. (2) and are given in Table 1. The acid dissociation and decomposition rate constants of xanthic acids were obtained by the analysis of log κ as a function of pH according to Eq. (1). Results are given in Table 2.

TABLE 1. LOG-VALUE OF κ/min^{-1} AS A FUNCTION OF pH

Methyl xanthate		Ethyl xanthate		Propyl xanthate		1-Methylethyl xanthate		Butyl xanthate		2-Methylpropyl xanthate	
pH	log κ	pH	log κ	pH	log κ	pH	log κ	pH	log κ	pH	log κ
1.23	1.47	1.23	1.39	1.23	1.40	1.20	1.35	1.17	1.40	1.20	1.17
1.57	1.39	1.57	1.33	1.57	1.34	1.73	1.31	1.70	1.33	1.70	1.12
1.76	1.32	1.76	1.29	1.76	1.31	2.00	1.26	2.40	1.05	1.95	1.10
1.99	1.21	1.99	1.20	1.99	1.23	2.20	1.14	2.70	0.83	2.23	0.98
2.52	0.84	2.52	0.90	2.52	0.97	2.65	0.87	3.25	0.39	2.70	0.72
2.75	0.63	2.75	0.68	2.75	0.79	2.94	0.68	3.45	0.16	2.95	0.53
2.93	0.57	2.93	0.63	2.93	0.65	3.06	0.56	4.07	−0.40	3.15	0.38
4.45	−0.89	4.47	−0.83	4.50	−0.89	4.47	−0.81	4.50	−0.82	4.50	−0.92
5.08	−1.49	5.11	−1.50	5.19	−1.50	5.08	−1.45	5.28	−1.62	5.08	−1.44
5.80	−2.24	5.82	−2.21	5.84	−2.19	5.80	−2.17	5.82	−2.18	5.84	−2.20

(2) Formation Constant of Metal Xanthato Complex. The polarographic determination of the compositions and the formation constants of the cadmium and zinc xanthato complexes was carried out by using Lingane's equation:[8)]

$$(E_{1/2})_s - (E_{1/2})_c = \frac{2.303RT}{nF}\log\beta_j + j\frac{2.303RT}{nF}\log[X^-], \qquad (3)$$

assuming the activity and diffusion coefficients of the simple and complexed metal ions to be equal to each other; where n is the number of moles of electrons involved in the electrode reaction, F the faraday, R the gas constant, T the absolute temperature, j the number of ligands coordinated to metal ion, and β_j the overall formation constant of MX_j. $(E_{1/2})_s$ and $(E_{1/2})_c$ denote the half-wave potentials of the simple and complexed metal ions, respectively.

The effect of pH on the diffusion current and the half-wave potential of simple metal ions was preliminarily studied. The half-wave potential was not affected by pH but the diffusion current decreased in a higher pH region than 8.2 for cadmium ion and 7.5 for zinc ion. Polarography for the metal xanthato complexes was therefore carried out in the pH ranging from 7.0 to 8.0 for the cadmium(II) system and from 7.0 to 7.3 for the zinc(II) system. The reversible half-wave potential was obtained graphically by the method of Matsuda and Ayabe.[9)]

As shown in Figs. 1 and 2, there was a linear relationship between the half-wave potential and the logarithm of the free xanthate ion concentration which was estimated by subtracting three times of metal concentration from the total concentration of xanthate. The values of the slope of these plots obtained for the cadmium(II) system were 90, 88, 91, 89, 88, and 89 mV for methyl, ethyl, propyl, 1-methylethyl, butyl, and 2-methylpropyl xanthates, respectively. And the values for the zinc(II) system were 85, 93, 96, 95, 94, and 91 mV, respectively. These values of the slope were in agreement with those expected from Eq. (3) in which j was 3. The overall formation constants, β_3, calculated from Eq. (3) are given in Table 2.

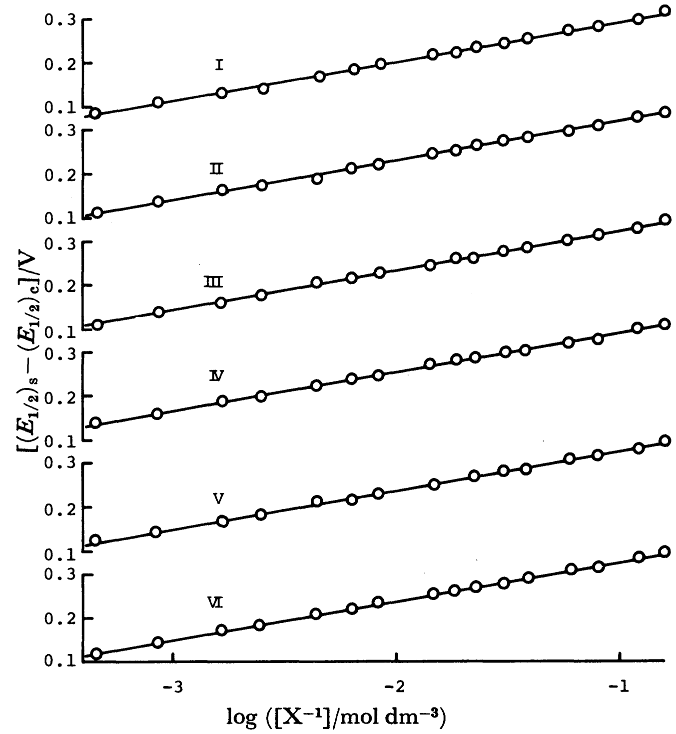

Fig. 1. Shift in the half-wave potential of cadmium(II) ion by the presence of alkyl xanthates in the 1 : 1 v/v water–DMF mixture.
I: methyl xanthate, II: ethyl xanthate, III: propyl xanthate, IV: 1-methylethyl xanthate, V: butyl xanthate, VI: 2-methylpropyl xanthate.

One of the authors (K. H.) has already studied the formation of ethyl xanthato complexes of cadmium and zinc in the 1 : 1 v/v water–DMF medium.[10)] According to him, the β_3 values for cadmium and zinc complexes were $10^{14.40}$ and $10^{4.63}$, respectively. The β_3 value for cadmium in Table 2 was in fair agreement with the above value, but the β_3 value for zinc complex obtained in this work was significantly larger than that reported previously. In the previous paper, lithium perchlorate (0.5 mol dm^{-3})–potassium nitrate (1.0—1.5 mol dm^{-3}) was used as the supporting electrolyte for the cadmium system, while potassium chloride (0.5—1.0 mol dm^{-3})

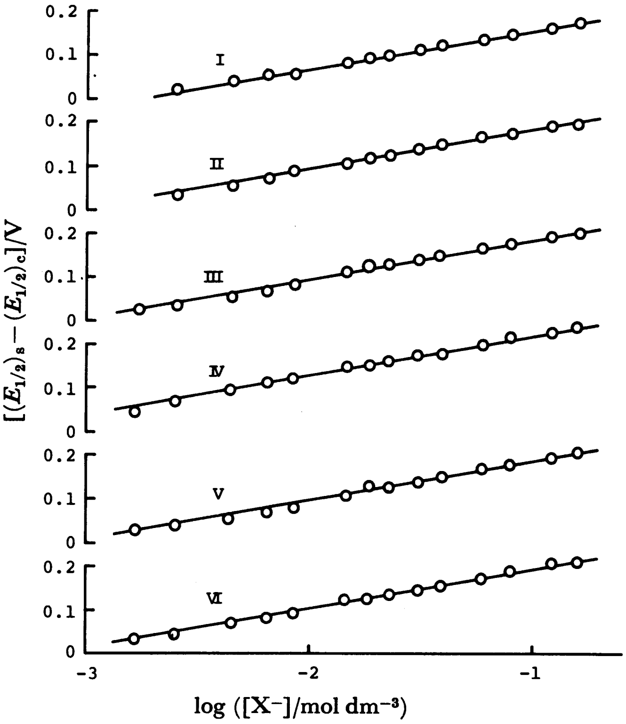

Fig. 2. Shift in the half-wave potential of zinc (II) ion by the presence of alkyl xanthates in the 1 : 1 v/v water-DMF mixture.

I: methyl xanthate, II: ethyl xanthate, III: propyl xanthate, IV: 1-methylethyl xanthate, V: butyl xanthate, VI: 2-methylpropyl xanthate.

was employed for the zinc system. Therefore, the apparent inconsistency seems to be caused by the formation of a zinc–chloro complex which was not considered in the previous paper.

As shown in Table 2, the basicity of xanthates increased in the order, methyl<ethyl<propyl<butyl<2-methylpropyl<1-methylethyl. This order is in agreement with the order reported in the aqueous medium[11] except for 2-methylpropyl and 1-methylethyl derivatives. The stability of complexes increased in the same order of the basicity of the ligands (Table 2), and this result is quite reasonable because a metal ion should form a more stable complex with a more basic ligand.

TABLE 2. ACID DISSOCIATION CONSTANT(K_a) AND DECOMPOSITION RATE CONSTANT(k_3) OF ALKYL XANTHIC ACID, AND FORMATION CONSTANT(β_3) OF CADMIUM AND ZINC XANTHATO COMPLEXES

Xanthate	pK_a	$\frac{k_3}{\text{min}^{-1}}$	log β_3 (for Cd)	log β_3 (for Zn)
Methyl	2.07	32.4	12.86	8.05
Ethyl	2.20	26.3	13.87	8.93
Propyl	2.22	27.5	13.94	9.00
1-Methylethyl	2.44	14.8	14.55	10.15
Butyl	2.23	27.5	14.04	9.04
2-Methylpropyl	2.25	26.9	14.04	9.20

The decomposition rate constant of methyl xanthate was the maximum and that of 1-methylethyl derivative was the minimum, and it can be said roughly that more basic xanthate is more stable in an acid solution.

The complexes of cadmium are always more stable than the corresponding zinc complexes. The difference in log β_3 was about 4.8. As cadmium(II) ion is more "soft" as Lewis acid than zinc(II) ion, the former should give a more stable complex with xanthate which coordinates through two sulfur atoms.

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