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The Formation Constants of Some Metal Thiobenzoato- and Thioacetato-Complexes in Dioxane-Water Solvent

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Recently the metal complexes of sulfur-containing ligands have been actively studied and many papers have been published. However, only a few data about their stability in the solution state have been obtained because of their low solubilities in water or their instabilities in a solution due to solvolytic decomposition.

Monothiocarboxylic acid is one of the most interesting sulfur-containing ligands, and solid metal complexes of monothio-benzoic acid have recently been synthesized and investigated by several authors.[1–3] Although they are insoluble in water, some of them are soluble in a 60% dioxane-water solution. Therefore, it seemed that it would be interesting to obtain their formation constant data.

The nickel(II), cobalt(II), manganese(II), zinc(II), and iron(II) complexes of thiobenzoic acid as well as thioacetic acid were investigated. When the copper(II) salt was mixed with the thiocarboxylic acid, an insoluble copper(I) complex has precipitated immediately. In the run using cadmium(II) salt, the equilibrium was not obtained even after it had stood 2 hr; after that turbidity was observed in the solution. Consequently, the formation constants of neither copper(II) nor cadmium(II) complexes were obtained.

Experimental

Materials. The 1,4-dioxane was a G. R. reagent of the Wako Chemical Co., Ltd., and was used after being purified according to the directions of Riddich and Toops.[4] The thiobenzoic acid and thioacetic acid used were G. R. reagents of the Tokyo Kasei Chemical Co., Ltd., while the other chemicals used were G. R. reagents of the Wako Chemical Co., Ltd.; they were used without any further purification.

General Procedure. The techniques employed were those of Calvin.[5] A Toa Denpa Co. model HA-5A pH meter, a glass electrode, and a saturated calomel electrode were used. All the measurements were made at 30.0±0.1°C. Each run was repeated 4 times, and the average values were used for the calculations.

The Measurement of the Acid-dissociation Constants. 30 m*l* of dioxane, 5 mmol of potassium nitrate, and 1 mmol of thiocarboxylic acid were diluted to 50 m*l* with water.[6] The sample was titrated with a 1.000 N sodium hydroxide standard aqueous solution. From the reading of the pH meter of the half-neutralized point (B), the pK_D (where K_D is the acid dissociation constant) was obtained by the Uitert's equation, $pK_D = B + (\log U_H^0 + \log 1/\gamma)$ (where U_H is a conversion factor obtained by the diagram of the authors).[7]

The Measurement of Formation Constants of the Complexes. 30 m*l* of dioxane, 4 mmol of potassium nitrate, 1 mmol of nitric acid, 0.1 mmol of metal nitrate (the sulfate was used in the cases of iron(II) salt), and 1 mmol of the ligand were mixed and diluted to 50 m*l* with water. The sample solution was left in a thermostat bath more than 3 hr in order to attain the equilibrium state. The titration of the sample was done over a 6 hr period after the dissociation in order to avoid the effect of the decomposition of the solute.

No precipitation was found during the ($n<2$) process. The calculation of the formation constants was done as has been described by Calvin,[5] Uitert,[7–9] and Goldberg.[10]

Results and Discussion

A typical run of the data and the results of the calculation are shown in Table 1. The acid dissociation constants obtained and the formation constants of their complexes are shown in Table 2.

Generally, the thiobenzoates are slightly more stable than the thioacetates of the corresponding metals.

Table 1. Titration of 60% dioxane-water solution of nickel nitrate (2.00×10^{-2}M), thiobenzioc acid (2.00×10^{-2}M), potassium nitrate (8.00×10^{-3}M), and nitric acid (2.00×10^{-3}M) with standard aqueous solution of sodium hydroxide (1.00N)

NaOH (m*l*)	B	$\bar{n}$	p(Ch$^-$)
1.050	3.96	0.54	4.30
1.100	4.20	1.00	4.09
1.150	4.40	1.44	3.91
1.200	4.65	1.91	3.69

B: Reading of the pH meter standardized with aqueous buffer.
(Ch$^-$): Mole concentration of the monovalent chelate anion Ch$^-$.
$\bar{n}$: The number of the coordinated ligand molecules per one metal ion.

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6) As the sample was titrated with a sodium hydroxide aqueous solution, each calculation was carried out using the U_H^0 (conversion factors) and values of each dioxane concentration, assuming that the total volume was obtained by the addition of the two. In these regions, the difference of $(U_H^0 + \log 1/\gamma)$ per 1% difference in the dioxane concentration is about 0.02. In Table 2, the concentration of dioxane is abbreviated to 60%, even though the precise values at 60% are expected to be in the range of ±0.02.

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Table 2. The dissociation constants and the formation constants of metal complexes of thiobenzoic acid and thioacetic acid in 60% dioxane[6] at 30°C

	Thiobenzoic acid		Thioacetic acid	
	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
H	-7.3_4		-7.6_1	
Mn(II)	4.1	3.5	4.1	3.5
Fe(II)	4.3	3.8	4.2	3.8
Co(II)	4.3	3.9	4.0	3.5
Ni(II)	4.3	3.9	4.1	3.6
Zn(II)	5.4	4.5	4.8	4.1

The formation constants of manganese(II), iron(II), nickel(II), and cobalt(II) were almost all the same, but that of the zinc(II) complex was a little higher, when the ligand acid was the same. According to Savant,[1] in the nickel(II) and zinc(II) complexes of thiobenzoic acid, the ligand acts as the bidentate and coordinates to the central metal *via* oxygen as well as *via* the sulfur atom of the ligand. Although the complexes of some of the metals used in this experiment have not yet been obtained in the solid state, they are expected to be in almost a very similar form in the solution. These complexes may be solvetad by dioxane, as in the case of pyridine adduct shown by Melson.[2] In the calculations, however, it is assumed that the thiocarboxylic acid will coordinate far more strongly than dioxane. According to Yamasaki,[11] the formation constants of nickel(II) and zinc(II) benzoate in an aqueous solution are slmost the same. On the other hand, Yamasaki,[12] Leussing,[13] and Freiser[14] have reported that zinc(II) makes a more stable complex than does nickel(II) when the ligand bonds to the central metal with charged sulfur.

Therefore, from these results, it seems that the sulfur atom of the thiocarboxylato complexes of these metals is likely to bond to the central metal even in a solution.

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