The Fluorometric Determination of Indium with 8-Quinolinethiol[1)]

Kunihiro WATANABE, Akio FUJIWARA, and Kyōzō KAWAGAKI

Faculty of Science and Technology, Science University of Tokyo, Yamazaki, Noda-shi, Chiba 278

(Received October 7, 1976)

8-Quinolinethiol reacts with indium in the presence of acetic acid to give a yellow ternary complex. The complex, which has a greenish-yellow fluorescence with an emission maximum at 515 nm, can be extracted into chloroform at pH 2—4. In the ternary complex, the fluorescence intensity was about two times as large as that of the indium 8-quinolinethiolato complex containing no acetate ion. The fluorescence was stable for at least 1 h. By the use of a 0.2 μg/ml uranine solution as the setting reagent, 0—25 μg of indium in 10 ml of chloroform was determined. The coefficient of the variation was 3% for 12 μg of indium. The extractability of the ternary complex from 50 ml of an aqueous solution into 10 ml of chloroform was 99%. Iron, mercury, and silver, which interfere with the determination of indium, were masked with ascorbic acid, potassium iodide, and thiourea. Other interfering elements, including zinc, cadmium, gallium, nickel, palladium, cobalt, antimony, gold, copper, bismuth, and vanadium, must be removed before any analysis.

8-Quinolinethiol reacts with metal ions to form water-insoluble chelates, and they are extracted into some organic solvents. The indium 8-quinolinethiolato chelate extracted into chloroform or benzene has been used in spectrophotometric[2)] and fluorometric[3,4)] determination methods. The spectra and the composition of the indium chelate have also been obtained by Davis.[3)] Suprunovich *et al.*[5)] found that the indium 8-quinolinethiolato chelate reacts with acetic acid to form a ternary complex. However, the determination of indium in terms of the ternary-complex formation has not yet been studied. Recently, the present authors have found the ternary complex of indium–8-quinolinethiol–acetic acid to have a stronger fluorescence than the indium 8-quinolinethiolato chelate containing no acetate ion.

The present paper will report on the fundamental conditions for the fluorometric determination of indium with 8-quinolinethiol in the presence of acetic acid. Chloroform and methyl isobutyl ketone (MIBK) were used as the extraction solvents.

Experimental

Reagents. Standard solution of indium: 0.2502 g of 99.99% indium metal (Mitsubishi Kinzoku) was dissolved in 25 ml of hydrochloric acid, and then the solution was diluted to 250 ml with water. The solution was diluted further as a more diluted solution was required.

0.2% 8-Quinolinethiol Solutiol: In 50 ml of 6 M (M=mol dm^{-3}) hydrochloric acid, 0.1 g of 8-quinolinethiol hydrochloride (Dojin Yakukagaku) was dissolved.

Buffer Solution: A 2% ammonium acetate solution was prepared. The pH of the buffer solution was adjusted with hydrochloric acid or ammonia.

Acetic Acid: Glacial acetic acid of an analytical grade (Wako Chemicals Co.) was used.

A 0.2 μg/ml Uranine Solution: 0.1 g of uranine was dissolved in water, and the solution was diluted to 100 ml. The solution was then further diluted with water to obtain a solution containing 0.20 μg uranine per ml.

Other Reagents: The chloroform and MIBK used as extraction solvents and the other chemicals used were all of an analytical reagent grade.

Apparatus. The fluorometric measurements were carried out using a Hitachi fluorescence spectrophotometer, Model 203, with a mercury lamp. A 120-W Xenon lamp was used as the exciting source for the measurements of the fluorescence and excitation spectra. A 1 cm × 1 cm quartz cell was used. The pH was measured with a Toa Denpa Model HM-5 pH meter. An Iwaki KM shaker was used.

Procedure. To a sample solution containing 0.5—25 μg of indium, we added 10 ml of glacial acetic acid and 0.2 ml of a 0.2% 8-quinolinethiol solution. After the solution had then been diluted to 50 ml with water, the pH of the solution was adjusted to 2.5 with diluted hydrochloric acid or ammonia. The resultant aqueous solution was then transferred into a separatory funnel. The indium complex was extracted with 10 ml of chloroform or MIBK by shaking it vigorously for 2 min. After the separation of the mixture into two phases, the organic phase was transferred into a quartz cell and the fluorescence intensity of the extract was measured using a 0.2 μg-per-ml uranine solution as the reference standard. The excitation and fluorescence wavelengths used were 365 and 515 nm respectively. The content of indium was calculated using the calibration curve.

Results and Discussion

Excitation and Fluorescence Spectra. The apparent excitation and fluorescence spectra of the ternary complex and the indium 8-quinolinethiolato chelate extracted into chloroform and MIBK are given in Fig. 1. The ternary complex had an excitation maximum at 395 nm and a fluorescence maximum at 515 nm, while the indium 8-quinolinethiolato chelate had an excitation maximum at 395 nm and a fluorescence maximum at 505 nm. No shift of these maximum wavelengths due to extraction solvents was observed. The ternary complex, however, had a fluorescence intensity about two times as large as that of the indium 8-quinolinethiolato chelate. The fluorescence intensity of the complex extracted into chloroform was greater than that of the complex extracted into MIBK.

Effect of the pH. The effect of the pH of the aqueous phase on the fluorescence intensity is shown in Fig. 2. The optimum pH for the extraction of the indium 8-quinolinethiolato chelate was 1.6. The maximum extractability of the ternary complex into chloroform was, however, obtained at pH values from 2 to 4 and the fluorescence intensity of the complex in MIBK gave a maximum at pH 1.8—2.2. Therefore, the extractions of the ternary complex were carried out at pH 2.5 in chloroform and at pH 2.0 in MIBK.

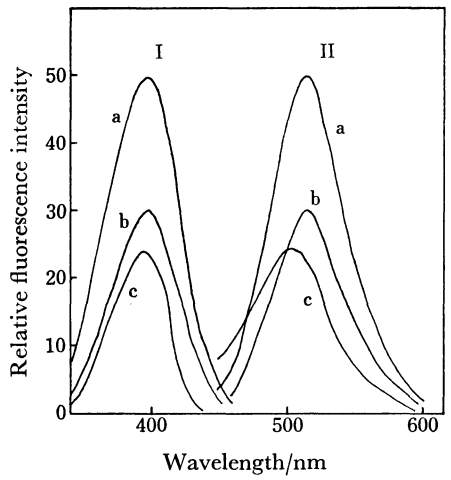

Fig. 1. Excitation and fluorescence spectra of indium complexes. Excitation spectra (I): Excited with xenon lamp and analyzed at wavelength for maximum fluorescence intensity. Emission spectra (II): Excited at 395 nm, a: acetic acid 10 ml, chloroform extraction, pH: 2.5, b: acetic acid 10 ml, MIBK extraction, pH: 2.0, c: acetic acid 0 ml, chloroform extraction, pH: 1.6, In 12 μg.

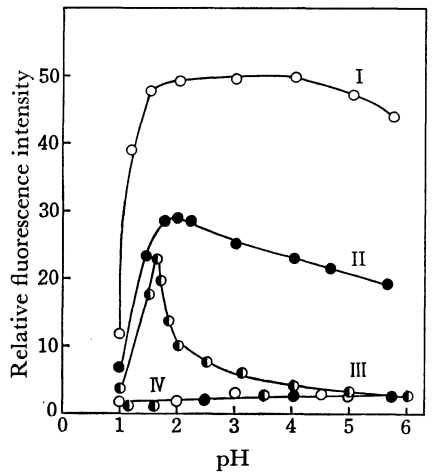

Fig. 2. Effect of pH on fluorescence intensity. In: 12 μg, I: acetic acid 10 ml, chloroform extraction, II: acetic acid 10 ml, MIBK extraction, III: acetic acid 0 ml, chloroform extraction, IV: reagent blanks.

Effect of the Acetic Acid Concentration. The effect of the acetic acid concentration in the aqueous phase on the extraction of ternary complex was examined by varying the acetic acid concentration. As the concentration of the acetic acid increased, the fluorescence intensity of the extract increased remarkably. However, above 3.4 M (10 ml acetic acid/50 ml) the fluorescence intensity increased gradually with the amount of acetic acid, as is shown in Fig. 3. On the other hand, since acetic acid in concentrations higher than 6.8 M gave difficulties in the pH adjustment and in the separation of the aqueous and MIBK phases, the concentration of acetic acid was kept at 3.4 M.

Effect of the Concentration of 8-Quinolinethiol. The effect of the 8-quinolinethiol concentration in the aqueous phase on the extractability of the ternary

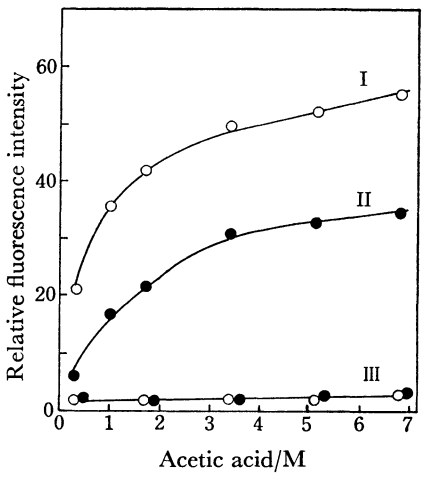

Fig. 3. Effect of the concentration of acetic acid on fluorescence intensity. In: 12 μg, I: chloroform extraction, II: MIBK extraction, III: reagent blanks.

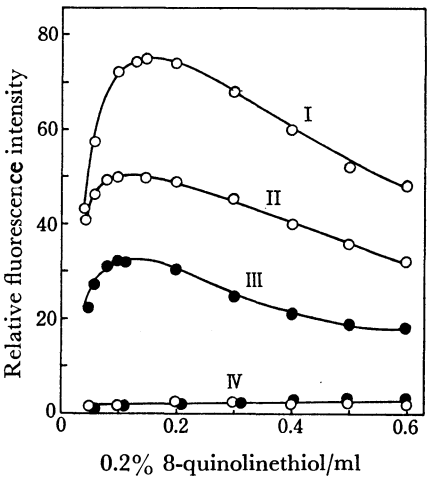

Fig. 4. Effect of amount of 8-quinolinethiol on fluorescence intensity. I: chloroform extraction, In: 18 μg, II: chloroform extraction, In: 12 μg, III: MIBK extraction, In: 12 μg, IV: reagent blanks, Acetic acid: 10 ml.

complex was examined by varying the amount of the 0.2% 8-quinolinethiol solution added, while the other variables were held constant. The results shown in Fig. 4 indicate that the optimum amount of the reagent was 0.1 ml of the 0.2% solution for 12 μg of indium, and from 0.1 to 0.2 ml for 18 μg of indium. The fluorescence intensity of the extracts decreased gradually with the increase in the reagent. The reagent blank was constant. Therefore, the amount of the 0.2% 8-quinolinethiol solution was kept at 0.2 ml.

Effect of the Volume of the Aqueous Solution. For the investigation of the effect, the volume of the organic phase was kept at 10 ml, while that of the aqueous phase was varied from 30 to 150 ml. When the concentration of acetic acid added was kept at 3.4 M, the fluorescence intensity in chloroform was nearly constant regardless of the increase in the volume of the aqueous phase. On the other hand, when MIBK was used for the extraction of the complex, a small amount of MIBK dissolved in the aqueous phase, so that the fluorescence

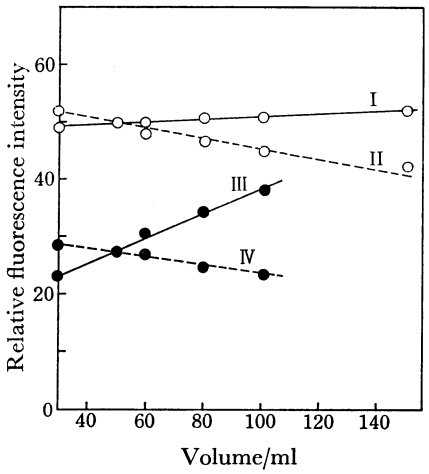

Fig. 5. Effect of volume of aqueous solution on fluorescence intensity. I, III: Concentration of acetic acid was kept at 3.4 M, II, IV: amount of acetic acid added was kept at 10 ml, I, II: chloroform extraction, III, IV: MIBK extraction.

intensity gradually increased with the volume of the aqueous phase. However, when the amount of acetic acid added was kept at 10 ml, the fluorescence intensities in organic solvents decreased with a decrease in the concentration of acetic acid. The results are shown in Fig. 5.

Effect of the Shaking Time, and the Stability of the Ternary Complex. The shaking time was varied from 0.25 to 30 min. It was found that shaking for 1 min was, in most cases, long enough for the extraction. A shaking time of 2 min was chosen, however, taking into consideration the possibility of accidental failure in extractability.

The fluorescence intensity of the ternary complex in a closed quartz cell was measured at 5 min intervals. The fluorescence intensity was constant until 10 min, past which point it increased gradually with the decrease in the amount of the solvent because of evaporation. However, after the ternary complex had been extracted, the fluorescence was stable at least for 60 min in a separatory funnel. It is recommended, therefore, to measure the fluorescence intensity of the complex within 10 min after it is transferred into a quartz cell.

TABLE 1. RELATIVE FLUORESCENCE INTENSITIES OF THE INDIUM–8-QUINOLINETHIOL–ACETIC ACID COMPLEX IN VARIOUS ORGANIC SOLVENTS

Solvent (10 ml)	Relative fluorescence intensity		
	Complex	Reagent blank	Difference
Chloroform	49.1	2.0	47.1
Benzene	31.8	1.2	30.6
MIBK	30.7	2.2	28.5
Toluene	27.0	1.8	25.2
Carbon tetrachloride	24.8	1.2	23.6
Xylene	26.1	2.9	23.2
Diisopropyl ether	23.0	1.2	21.8
Cyclohexane	4.0	1.2	2.8

In: 12 μg.

Extractability. A 50 ml portion of the aqueous phase containing the indium complex was shaken with 10 ml of chloroform, and the fluorescence intensity of the extract was measured. Then the indium remaining in the aqueous phase was extracted twice with chloroform. Extractability was calculated from the sum of the fluorescence intensities of the extracts and that of the first extract. It was found that 99% of indium was extracted by a single extraction.

Choice of Solvent. Chloroform was used as the extraction solvent of indium 8-quinolinethiolato chelate by Davis,[3] while benzene was used by Korenman *et al.*[4] The ternary complex of indium–8-quinolinethiol–acetic acid can also be extracted into many organic solvents. Therefore, the relative fluorescence intensities of the ternary complex extracted into several organic solvents were examined. The experimental results showed that chloroform and benzene, as well as MIBK, were excellent solvents, as is shown in Table 1. Chloro-

TABLE 2. EFFECTS OF DIVERSE IONS

Ion	(mg)	Added as	In found (μg)
Al^{3+}	8.0	$Al(NO_3)_3 \cdot 9H_2O$	12.0
Na^{+}	8.0	NaCl	12.0
Mg^{2+}	8.0	$Mg(NO_3)_2 \cdot 6H_2O$	12.0
Ca^{2+}	8.0	$Ca(NO_3)_2 \cdot 4H_2O$	12.0
Ba^{2+}	8.0	$BaCl_2 \cdot 2H_2O$	12.0
Cr^{3+}	8.0	$Cr(NO_3)_3 \cdot 9H_2O$	12.0
Sr^{2+}	8.0	$Sr(NO_3)_2$	11.9
Zr^{4+}	4.0	$ZrOCl_2 \cdot 8H_2O$	12.0
Cu^{2+}	0.01	$CuSO_4 \cdot 5H_2O$	12.0
	0.02	$CuSO_4 \cdot 5H_2O$	10.5
Ag^{+}	0.061	$AgNO_3$	10.9
	1.0	$AgNO_3$+10% thiourea 1 ml	12.0
Hg^{2+}	0.1	$Hg(NO_3)_2 \cdot 1/2H_2O$	5.0
	0.1	$Hg(NO_3)_2 \cdot 1/2H_2O$+10% ascorbic acid 1 ml+2N KI 2 ml	11.8
Fe^{3+}	0.042	Fe+HNO_3	9.5
	1.0	Fe+HNO_3+10% ascorbic acid 1 ml	12.0
Ni^{2+}	0.023	Ni+HNO_3	9.8
Co^{2+}	0.011	$Co(NO_3)_2 \cdot 6H_2O$	9.5
Cd^{2+}	0.06	Cd+HNO_3	12.0
	0.148	Cd+HNO_3	13.2
Zn^{2+}	0.006	Zn+HCl	17.6
Ga^{3+}	0.015	Ga_2O_3+HCl	24.3
Mn^{2+}	1.0	$MnCl_2$	12.0
Tl^{+}	8.0	$TlNO_3$	12.4
Pb^{2+}	5.0	Pb+HNO_3	12.5
Sn^{2+}	0.2	$SnCl_2 \cdot 2H_2O$+HCl	11.9
Bi^{3+}	0.05	$Bi(NO_3)_3 \cdot 5H_2O$	9.9
	0.1	$Bi(NO_3)_3 \cdot 5H_2O$	6.3
Sb^{3+}	0.07	Sb+H_2SO_4	12.0
	0.3	Sb+H_2SO_4	6.6
As^{3+}	5.0	As_2O_3+NaOH	12.0
Pd^{2+}	0.04	$PdCl_2$+HCl	3.0
La^{3+}	0.6	La_2O_3+HCl	12.4
Au^{3+}	0.046	$HAuCl_4 \cdot 4H_2O$	6.5
W^{6+}	8.0	$Na_2WO_4 \cdot 2H_2O$	12.0
V^{5+}	0.04	NH_4VO_3	5.2

In taken: 12.0 μg; 0.2% 8-quinolinethiol 0.2 ml; pH 2.5.

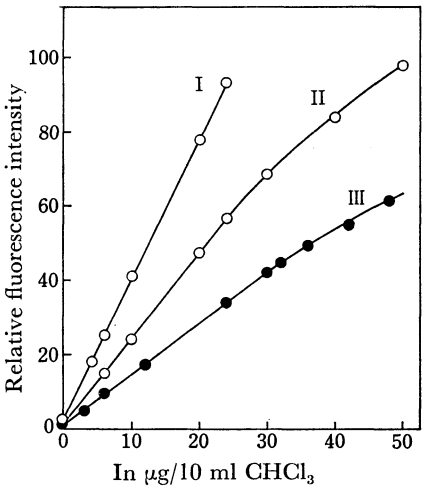

Fig. 6. Calibration curves for indium. Fluorometer reading was set at 50 div. (curve I) or 30 div. (curves II, III) with the uranine reference solution (0.2 μg/ml). I, II: chloroform extraction, III: MIBK extraction.

form and MIBK have been chosen as the solvents.

Calibration Curves. Figure 6 shows the calibration curves for indium, which were obtained by the described procedure above, based on the experimental results. However, the pH's of extraction were 2.5 in the chloroform extraction and 2.0 in the MIBK extraction. The sensitivity of the fluorometer was adjusted by setting the fluorescence of the standard uranine solution (0.2 μg/ml) at 30 or 50 on the fluorometer scale.

A good linear relationship was obtained over the concentration ranges from 0 to 25 μg per 10 ml of chloroform, and from 0 to 32 μg per 10 ml of MIBK. The coefficient of the variation obtained in 25 measurements was 3% for 12 μg of indium.

Effects of Diverse Ions and of Masking. The effects of 29 cations on the determination of indium were studied under optimum conditions. The results are shown in Table 2. Gallium, zinc, and cadmium gave positive errors in the determination of indium, and copper, cobalt, iron, nickel, palladium, mercury, bismuth, antimony, gold, vanadium, and silver ions reduced the fluorescence, but the other ions presented in Table 2 did not interfere.

The interference of ions such as iron (up to 1 mg), mercury (up to 100 μg), and silver (up to 1 mg) can be masked by using ascorbic acid, a mixture of ascorbic acid and potassium iodide, and thiourea respectively.

Composition of the Ternary Complex. By using the variation method fluorometrically, the molar ratio of indium to 8-quinolinethiol was found to be 1 : 2. However, the molar ratio of indium to acetic acid was not determined.

References

1) Determination of metals with thiooxine. VI. Part V of this series: K. Watanabe and K. Kawagaki, *Bunseki Kagaku*, **25**, 246 (1976).

2) J. Bankovskis, J. Cirule, and A. Ievins, *Zh. Anal. Khim.*, **16**, 562 (1961).

3) R. Davis, *Univ. Microfilms* (Ann Arbor. Mich.), Order No. 66-7874.

4) I. M. Korenman, F. R. Sheyanova, and N. I. Starodubova, *Tr. Po Khim. i Khim. Tekhnol.*, **1963**, 243.

5) V. I. Suprunovich and Yu. I. Usatenko, *Ukr. Khim. Zh.*, **34**, 120 (1968).