Color Reaction between Indium(III) and *o*-Hydroxyhydroquinonephthalein, and Its Application

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Synopsis. Color reaction between indium(III) and *o*-hydroxyhyroquinonephthalein(Qnph) in the presence of a cationic surfactant was studied, and its application for the spectrophotometry and photometric titration of indium(III) was discussed. The color reaction between Qnph and indium(III) in the presence of hexadecyltrimethylammonium chloride(HTAC) was stable in weakly acidic media. The calibration curve was rectilinear in the range of 0—10 μg/10 cm³ of indium(III) at 560 nm, and the apparent molar absorption coefficient was 1.3×10^5 dm³ mol⁻¹ cm⁻¹. The Sandell sensitivity was 0.0008 μg/cm² for indium(III).

For the detection and determination of indium(III) various methods using oxine, dithizone, Xylenol Orange(XO), Methylthymol Blue(MTB), Pyrocatechol Violet(PV), etc. have been reported.[1-11] However, most of these methods are complicated and/or not sufficiently sensitive. The color formation between *o*-hydroxyhydroquinonephthalein(Qnph) and indium(III) in the presence of hexadecyltrimethylammonium chloride(HTAC) as a cationic surfactant was sharp, stable and gave a larger absorbance than the color reaction without surfactant.

In this paper, the color reaction between Qnph and indium(III) was discussed, and then a simple, rapid and sensitive spectrophotometric method for the determination of indium(III) was established.

Experimental

Apparatus and Reagents. Spectrophotometric measurements were carried out on Shimadzu Model UV—200, UV-240 and Hitachi Model 150-20 recording spectrophotometers with 1.0-cm fused silica cells. A Shimadzu Model QV-50 spectrophotometer and its attachments were used for photometric titration of indium(III). Hitachi-Horiba Model F-7AD and M-5 glass electrode pH meters were used for the pH measurements.

A 1.0×10^{-3} mol dm^{-3} solution of Qnph was prepared according to the previous report.[12] The working solutions (5.0×10^{-4} mol dm^{-3}) of indium(III) and a 1.0×10^{-2} mol dm^{-3} EDTA solutions were prepared according to the previous reports,[9] respectively. A 2.0×10^{-2} mol dm^{-3} HTAC solution was prepared by dissolving HTAC in water, and a 2.0×10^{-1} mol dm^{-3} sodium acetate–acetic acid buffer solution was used for the pH adjustments. All the other reagents and materials were of analytical grade and were used without further purification. Doubly distilled water was used.

Standard Procedure. Spectrophotometric determination of indium(III): To a solution containing up to 10 μg indium(III) in a 10 cm³ volumetric flask were added 1.0 cm³ of a 2.0×10^{-2} mol dm^{-3} HTAC solution, 1.5 cm³ of a 1.0×10^{-3} mol dm^{-3} Qnph solution, and 2.0 cm³ of a 2.0×10^{-1} mol dm^{-3} acetate buffer solution(pH 5.4). The mixture was diluted to 10 cm³ with water(Solution B), and the solution was mixed well, and kept at room temperature for 10 min. The absorbance of Solution B was measured at 560 nm against the reagent blank(Solution A).

Photometric titration of indium(III): A solution containing less than 900 μg of indium(III) was placed in a tall beaker (40×90 mm); to this solution 5.0 cm³ of a 2.0×10^{-3} mol dm^{-3} HTAC solution and 1.5 cm³ of a 1.0×10^{-3} mol dm^{-3} Qnph solution were added. The pH of the solution was adjusted to about 3.5 with a 2.0×10^{-1} mol dm^{-3} sodium acetate-hydrochloric acid solution, was diluted to 30 cm³ with water, and was heated at 60—70 °C for 10 min. Then the mixed solution was titrated by a 1.0×10^{-2} mol dm^{-3} EDTA solution by measuring the absorbance at 560 nm or 520 nm. The concentrations of indium(III) were calculated from the relationship between the absorbance at 560 nm or 520 nm and the amounts used of a 1.0×10^{-2} mol dm^{-3} EDTA solution.

Results and Discussion

Color Reaction and Absorption Spectra. The color reaction between Qnph and indium(III) was studied in weakly acidic media with or without various kinds of surfactants——poly(oxyethylene)-sorbitan monolaurate (Tween 20) as a nonionic, HTAC as a cationic or sodium dodecyl sulfate(SDS) as an anionic surfactant. The Qnph-indium(III) complex solution in the presence of HTAC showed a considerable bathochromic shift with two times larger and more stable absorbance than the complex in the presence of Tween 20 or SDS.

Effects of pH and Surfactants. The maximum and constant absorbance was obtained in the pH range from 5.2 to 6.2 for indium(III) by addition of 2.0 cm³ of a 2.0×10^{-1} mol dm^{-3} Walpole acetate buffer solution in the final volume of 10 cm³. Among various surfactants, HTAC, hexadecylpyridinium chloride(HPC), zephiramine, HTAC, a cationic surfactant, was found to be the best as a dispersion agent. The maximum and constant absorbance could be obtained over the range of 0.5 to 2.0 cm³ of a 2.0×10^{-2} mol dm^{-3} HTAC solution to the final volume of 10 cm³. Subsequent measurement was carried out by addition of 2.0 cm³ of the buffer solution(pH 5.4) and 1.0 cm³ of a 2.0×10^{-2} mol dm^{-3} HTAC solution in the final volume of 10 cm³.

Effects of Qnph Concentration and Stability. The recommended concentration of Qnph was 1.5×10^{-4} mol dm^{-3} in the final solution. Under the conditions of the standard procedure, the maximum and almost constant absorbance was obtained by keeping the Qnph–indium(III) solution at room temperature for

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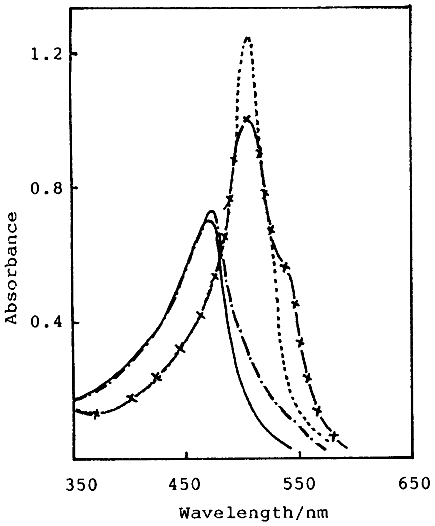

Fig. 1. Absorption spectra of Qnph and Qnph–indium(III) complex solutions in the presence of Tween 20 or HTAC at pH 5.4.
Indium(III): 4.0×10^{-6} mol dm^{-3}; Qnph: 4.0×10^{-5} mol dm^{-3}; HTAC: 2.0×10^{-3} mol dm^{-3}; Tewen 20 : 1.0 cm^3 of a 1.0% Tween 20 solution/10 cm^3; Reference : water.
——: Qnph-Tween 20 solution, — — —: Qnph-Tween 20-indium(III) solution, - - - -: Qnph-HTAC solution, —×—: Qnph-HTAC-indium(III) solution.

Table 1. Effects of Foreign Ions

Foreign ions	Added as	Added µg/10 cm^3	Absorbance at 560 nm
—	—	—	0.776
Bi(III)	Nitrate	1.6	0.980
Th(IV)	Nitrate	1.5	0.824
Al(III)	Nitrate	2.7	0.830
Fe(III)	Sulfate	1.5	0.850
Co(II)	Nitrate	1.6	0.845
Ni(II)	Nitrate	12.0	0.750
Cu(II)	Nitrate	1.6	0.820
Zn(II)	Nitrate	11.0	0.845
Ce(III)	Chloride	0.2	0.776
MoO_4^{2-}	Sodium	0.5	0.776
SCN^-	Ammonium	0.5	0.750
NO_2^-	Potassium	58.0	0.750
CN^-	Potassium	126.0	0.780
$C_2O_4^{2-}$	Sodium	180.0	0.750
Cl^-	Sodium	443.0	0.776
F^-	Sodium	23.7	0.776
$S_2O_3^{2-}$	Sodium	114.5	0.776
Citrate	Sodium	190.0	0.685
Tartrate	Sodium	15000.0	0.695

Indium(III) taken: 7.2 µg/10 cm^3; Qnph: 1.5×10^{-4} mol dm^{-3}; pH: 5.4; HTAC: 2.0×10^{-3} mol dm^{-3}: Reference: Reagent blank.

longer than 10 min. The absorbance was almost constant at least for 90 min.

Calibration Curve and Repeatability. The calibration curve for indium(III) was constracted according to the standard procedure. Beer's law held in the concentration range of 0—10 µg of indium(III) in the final volume of 10 cm^3. The apparent molar absorption coefficient was estimated to be 1.3×10^5 dm^3 mol^{-1} cm^{-1} at 560 nm, and the Sandell sensitivity was calculated to be 0.0008 µg cm^{-2} for indium(III). The coefficient of variation(n=5) for 7.2 µg indium(III) was 1.5%.

Effects of Foreign Ions. The tolerance limits were taken as the amount causing 2% error in the absorbance. The coexistence of small amounts of copper(II), iron(III), aluminum(III), bismuth(III), etc. showed positive errors because of the formation of a colored complex with Qnph. In 2—30 fold molar excess of indium(III), the interference of copper(II), aluminum(III), and iron(III) could be overcome to some extent by addition of sodium thiosulfate, nitrilotriacetic acid(NTA) or sodium fluoride and potassium cyanide or sodium fluoride solutions, respectively. Also, the interference of bismuth(III) could be overcome by addition of NTA in a 50-fold excess. Although the coexistence of large amounts of tartrate, citrate and oxalate ions, etc. interfered, the presence of most anions scarcely interfered in the 100—200 fold molar excess of indium(III). The results are summarized in Table 1.

The Composition of the Complex. The molar ratio of Qnph to indium(III) in the presence of HTAC was estimated to be 2:1 by the molar-ratio and the continuous-variation methods. On the other hand, the molar ratio of Qnph to indium(III) in the coexistence of Tween 20 without HTAC was 3:2 by the molar-ratio method. The molar ratio of HTAC to the indium(III)-Qnph solution was found to be 2:1 in the presence of nonionic surfactants.

Photometric Titration. At the end point of the photometric titration of indium(III) by using Qnph as a metal indicator at around pH 3—5 in the coexistence of HTAC the color changed from orange red to yellow. In the photometric titration of indium(III), the difference of absorbance at 560 or 520 nm of the Qnph–indium(III) solution and that of the Qnph solution was measured. The proposed method was well suitable for differential titration of the mixed metal ion solution (for example, indium(III)-bismuth(III), indium(III)-thorium(IV), indium(III)-aluminum(III)-cobalt(II), etc.).

The recovery of indium(III) added to a waste water involving of copper(II), cadmium(II), lead(II), zinc(II), aluminum(III), iron(III), bismuth(III), etc. was examined, and the results were satisfactory (98.5—103.0%).

In conclusion, the color reactions between indium(III) and Qnph in the presence of various surfactants were studied, and a simple, rapid and sensitive spectrophotometric determination of indium(III) was established by using the color reaction between Qnph and indium(III) in the presence of HTAC in weakly acidic media. The calibration curve was linear in the concentration range of 0—10 µg/10 cm^3 for indium(III). The apparent molar absorption coefficient was estimated to be 1.3×10^5 dm^3 mol^{-1} cm^{-1}. The sensitivity of this method was about 9 times greater than the oxine or MTB method,³⁾ and 3—4 fold greater than 1-(2-pyridylazo)-2-naphthol(PAN)²⁾ or previously reported method.⁹⁾ The effects of foreign ions were relatively smaller than the previous method.⁹⁾

Though further investigation is necessary, the proposed method may be useful for the determination of indium(III) in alloys, iron ores, semiconductors, etc.

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