Spectrophotometric Determination of Antimony(III) as Pyrocatechol Violet Complex with Tetraphenylphosphonium Chloride

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The spectra of antimony(III)-Pyrocatechol Violet(PV) complexes were given rise to bathochromic shifts about 100 nm by the addition of tetraphenylphosphonium cation in aqueous solution. An absorbance at 630 nm was little affected by that of reagent blanks and gave a good sensitivity for the spectrophotometric determination of antimony(III). The molar absorptivity was $16500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in the presence of $0.024 \text{ mol dm}^{-3}$ TPPC and $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ PV concentrations at the pH ranges from 2.5 to 4.5, and this solution was stable up to 20 h in the presence of 0.1% gum arabic.

Keywords Spectrophotometry, antimony(III), Pyrocatechol Violet, tetraphenylphosphonium ion, dispersant, solubilization

Pyrocatechol Violet (PV) in the triphenylmethane dyes formed color complexes with various metal ions and widely utilized as a spectrophotometric reagent.¹ There are some problems remained concerning with the sensitivity and selectivity. The absorption spectra of these complexes often overlapped that of PV itself. West and co-workers^{2,3} studied the effect of quaternary ammonium salts such as cetyltrimethylammonium bromide (CTAB) on the spectra of complexes and they observed the bathochromic shift in improving the sensitivity by the addition of CTAB. Furthermore, confusing spectral changes were also observed depending on the concentration of CTAB. Surfactants such as CTAB form the micelles in aqueous solutions above the critical micellar concentration. The complex will be extracted or solubilized in these micelles.

The spectral change of the triphenylmethane dyes and its metal complexes were very sensitive to the concentration or variety of surfactants in the spectrophotometry of metal ions.^{4,5} On the other hand, the absorption spectra of complexes also caused the bathochromic shift and gave the stable color when auxiliary reagents such as tetraphenylphosphonium chloride (TPPC) were added in the solution. TPPC could not form the micelle in aqueous solution. In the present paper, the spectrophotometric determination of antimony (III) was examined with PV and TPPC.

Experimental

Reagents

Water that had been deionized and distilled was used in the preparation of all solutions. A stock solution of antimony(III) was prepared by dissolving 0.3340 g of antimony potassium tartrate 0.5 hydrate (Wako pure chemicals) in 1.0 dm^3 of water.² Both $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ PV and 0.08 mol dm^{-3} TPPC (Dojindo laboratories) solutions were prepared by dissolving weighed amounts of reagents in water. Acetate buffer was prepared from 0.01 mol dm^{-3} acetic acid and 0.01 mol dm^{-3} sodium acetate, and its pH was adjusted to 3.9 with pH meter. A 1.0%(w/v) gum arabic (Wako Pure Chemicals) solution was prepared by dissolving 0.50 g in 50 cm^3 of the warmed water and filtered. All other chemicals were of analytical grade.

Apparatus

The spectra and absorbance were measured by a Shimadzu UV-240 recording spectrophotometer with 10 mm quartz cells. All pH measurements were made with a Horiba M-7 pH meter and a combination glass electrode. Some turbid solutions were centrifuged by a Kubota K-80 centrifuge.

General procedure

A sample solution involving less than $37 \text{ } \mu\text{g}$ of antimony(III) was placed in a 10 cm^3 volumetric flask.

After PV and gum arabic solutions were added, the solution was shaken slowly. TPPC and acetate buffer were successively added, then this solution was diluted to the mark with water and shaken slowly. The absorbance at 630 nm was measured against a reagent blank.

Results and Discussion

Optimization of the conditions for antimony(III) analysis

The curve A in Fig. 1 shows the absorption spectrum when TPPC was added in the aqueous solution involving antimony(III) and PV. The absorbance measurement at 630 nm was little affected by the

Fig. 1 Absorption spectra. [Sb(III)], 2.0×10^{-5} mol dm $^{-3}$; [PV], 2.0×10^{-4} mol dm $^{-3}$; [TPPC], 0.024 mol dm $^{-3}$; [CTAB], 5.48×10^{-4} mol dm $^{-3}$; gum arabic, 0.1%; pH 3.9; A, Sb(III)-PV-TPP against reagent blank; B, reagent blank against water; C, Sb(III)-PV-CTAB against reagent blank; D, Sb(III)-PV-TPP extracted in chloroform against reagent blank.

Fig. 2 Effect of pH. [Sb(III)], 2.0×10^{-5} mol dm $^{-3}$; [PV], 2.0×10^{-4} mol dm $^{-3}$; [TPPC], 0.024 mol dm $^{-3}$; gum arabic 0.1%; O, Sb(III)-PV-TPP against reagent blank; ●, reagent blank against water.

reagent blank. As shown in Fig. 2, the absorbance at 630 nm was a constant in the range of pH 2.5 to 4.5. The constant absorbance was obtained between 2.0×10^{-4} and 6.0×10^{-4} mol dm $^{-3}$ PV. At higher PV concentrations, the absorbance was not able to measure because of the formation of precipitate. The effect of TPPC concentrations is shown in Fig. 3. When TPPC was more than 0.012 mol dm $^{-3}$ the constant and maximum absorbance was obtained. This solution was unstable and became turbid with time, therefore some dispersants such as gum arabic were used. The effect of gum arabic concentrations was examined in the range of 0.01 to 0.1%. The solution was still stable after 20 h at the gum arabic concentration more than 0.03%. The calibration curve was followed by Beer's law in the range of 5.0×10^{-6} to 3.0×10^{-5} mol dm $^{-3}$ antimony(III) concentration. The apparent molar absorptivity was 16500 dm 3 mol $^{-1}$ cm $^{-1}$ and seven replicate absorbance measurements gave the relative standard deviation of 1.2%.

Interferences

The commonly interfering ions were added to the solution containing 24 μg antimony(III). Results are presented in Table 1. Equimolar amounts of ion(III) and aluminum(III) largely interfered because these ions formed the complexes with PV. Large amounts of cadmium(II) and lead(II) formed precipitates. Voluminous anions such as thiocyanate formed the ion-pairs with TPP cation and precipitated. Especially, TPP cation reacted with perchlorate ion to form a water-insoluble, stable precipitate and can be used as a gravimetric reagent.⁶ EDTA masked antimony(III) and caused the decrease of absorbance.

Solvent extraction

The anionic PV complex was also extractable with the TPP cation in organic solvents. The spectrum in

Fig. 3 Effect of TPPC concentration. [Sb(III)], 2.0×10^{-5} mol dm $^{-3}$; [PV], 2.0×10^{-4} mol dm $^{-3}$; gum arabic, 0.1%; pH 3.9; reference, water.

chloroform phase showed the absorption maximum at about 530 nm as well as that in the aqueous solution containing CTAB (C,D in Fig.1). The absorbance at 527 nm was constant in the range of pH 3.0 to 5.0, and concentration ranges of PV and TPPC from 5.0×10^{-5}

to 1.2×10^{-4} mol dm⁻³ and from 8.0×10^{-3} to 2.0×10^{-2} mol dm⁻³, respectively. The calibration graph examined with each 10 cm³ of aqueous and chloroform phases was followed by Beer's law in the range of 2.0×10^{-6} to 2.5×10^{-5} mol dm⁻³ antimony(III). The apparent molar absorptivity was 38000 dm³ mol⁻¹ cm⁻¹ and the absorbance was stable up to 3 h.

Previously, Tsukahara and co-workers⁷ also reported the extraction of the ion-pair of anionic antimony(III)-PV complex with trioctylamine into toluene and measured the traces of antimony in copper and lead metals at 555 nm. In the extraction-spectrophotometry of antimony(III) using TPP cation or trioctylamine the apparent molar absorptivities were about 2 times larger than that in the aqueous system. However, the absorption measurement were interfered by the reagent blank of PV extracting in the organic phases.

Table 1 Effect of foreign ions

Foreign ions	Added as	Molar excess relative to Sb	Absorbance
—	—	—	0.331
Mg(II)	sulfate	500	0.330
Co(II)	chloride	500	0.360
Ni(II)	nitrate	500	0.345
Al(III)	alum	0.05	0.334
		0.5	0.410
Fe(III)	alum	0.05	0.343
		0.5	0.392
Cu(II)	sulfate	5	0.358
Cd(II)	nitrate	5	0.330
		50	precipitation
Zn(II)	sulfate	500	0.341
Mo(VI)	ammonium	0.05	0.369
Pb(II)	nitrate	5	0.332
		50	0.420
Mn(II)	nitrate	500	0.348
NH ₄ ⁺	chloride	500	0.325
K ⁺	chloride	5000	0.321
tartrate	sodium	5	0.271
EDTA	sodium	0.5	0.277
NO ₃ ⁻	sodium	5000	0.325
Cl ⁻	sodium	5000	0.329
SCN ⁻	sodium	5	0.330
		50	0.492
Ascorbic acid		500	0.340
NO ₂ ⁻	sodium	0.5	0.311

Fig. 4 Effect of Triton X-100 or CTAB concentration on the absorbance at 630 nm. [Sb(III)], 2.0×10^{-5} mol dm⁻³; [PV], 2.0×10^{-4} mol dm⁻³; pH 3.9; O, Triton X-100; ●, CTAB.

Spectral change in surfactant solution

In the aqueous solution containing TPPC, the absorbance at 630 nm decreased with increase in the nonionic surfactant concentrations of Triton X-100 due to the solubilization of the complex into micelle (Fig. 4). When the sufficient amounts of Triton X-100 were added, the absorption maximum shifted from 630 nm to 530 nm. Therefore, the color of solution changed from blue to red. West and co-workers² carried out the spectrophotometry of antimony(III) with PV and CTAB and reported the formation of the red or blue complex depending on the CTAB concentrations. When the CTAB concentration was higher than that of PV, the red complex having absorption maximum at 530 nm was mainly formed in the solution. On the other hand, the blue complex was formed at very low CTAB concentrations. As shown in Fig. 4, the absorbance at 630 nm was highly sensitive to the concentration of CTAB. Consequently, they performed the measurement at 530 nm where the absorption of the reagent blank somewhat decreased in the sensitivity.

The monomer of cationic surfactants such as CTAB reacted as a counter ion of the ion-pair formation, however these ion-pairs will be extracted into micelle concurrently formed in the solution. The cation of TPP brought the bathochromic shift of spectra but couldn't make the micelle.⁴ However, the stable ion-pair with TPP cation liberated as the precipitate from the aqueous solution with time. The careful selection of an auxiliary dispersant provide the wide use for the spectrophotometry of many metals as the PV complexes.

References

1. K. L. Cheng, K. Ueno and T. Imamura, "Handbook of Organic Analytical Reagents", p. 35, CRC Press, Florida (1982).

2. B. W. Bailey, J. E. Chester, R. M. Dagnall and T. S. West, *Talanta*, **15**, 1359 (1968).
3. D. H. Christopher and T. S. West, *Talanta*, **13**, 507 (1966).
4. S. Tagashira, *Anal. Chim. Acta*, **157**, 343 (1984).
5. K. Hayashi, Y. Sasaki, S. Tagashira and E. Kosaka, *Anal. Chem.*, **58**, 1444 (1986).
6. T. Okubo, F. Aoki and T. Teraoka, *Nippon Kagaku Zasshi*, **89**, 432 (1968).
7. I. Tsukahara, M. Sakakibara and M. Tanaka, *Anal. Chim. Acta*, **92**, 379 (1977).

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