

# Study of Semisarosinexylenol Blus as Spectrophotometric Reagent : Determination of Iron (III)

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# Study of Semisarcosinexylenol Blue as Spectrophotometric Reagent

## —Determination of Iron(III)—

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### Summary

Semisarcosinexylenol Blue (SSXB) was synthesized and the usefulness of it as a spectrophotometric reagent was evaluated. SSXB forms colored complexes with indium, lead, copper, zinc, scandium, zirconium, thorium, iron(III), cobalt, and nickel, and can be used as photometric reagent of copper and iron(III) because of relatively strong coloration with these ions. With iron(III), this reagent forms a water-soluble reddish-violet complex. The composition of the complex is  $\text{Fe(III)(SSXB)}_2$ . The optimum pH range for the color development is 5.4–6.3 and the maximum absorption of the colored solution lies at 526–529 nm. The sensitivity of the determination and the molar absorptivity of the complex are  $3.7 \times 10^{-3} \mu\text{g cm}^{-2}$  of iron(III) for 0.001 of absorbance and  $1.54 \times 10^4$ , respectively. Beer's law is held up to  $1.4 \mu\text{g cm}^{-3}$  of iron(III). Among the twenty four diverse ions examined, copper, zirconium, tungsten(VI), cobalt, nickel, and tartrate interfere with the determination, but the effect of cobalt could be eliminated by the addition of hydrogen peroxide and the influence from copper could be also eliminated by the separation of copper as its ammine complex. This reagent also reacts with iron(III) in the presence of cetylpyridinium bromide (CPB) to form a water-soluble reddish-violet complex, increasing the sensitivity about 20% of that in the absence of CPB. The colored solution of the complex has an absorption maximum at 540–542 nm with almost constant absorbance at pH 3.9–5.7. The sensitivity of the determination is  $3.0 \times 10^{-3} \mu\text{g cm}^{-2}$  of iron(III) for 0.001 of absorbance and Beer's law is obeyed up to  $1.4 \mu\text{g cm}^{-3}$  of iron(III).

### Introduction

In a series of sulfophthalein derivatives, there are many useful compounds utilizing the spectrophotometric reagents for various metal ions.<sup>1,2)</sup> As a part of the investigation of the methods for the photometric determination of metal ions with sulfophthalein derivatives, the

author newly synthesized Semisarcosinexylenol Blue, 3-[N-(carboxymethyl) methylaminomethyl]-*p*-xylenolsulfophthalein, from Paraxylenol Blue and sarcosine by the Mannich condensation,<sup>1)</sup> purified it by cellulose column, and examined the color reactions with some metal ions. It was found that it is possible to use Semisarcosinexylenol Blue (SSXB) as the spectrophotometric reagent of copper and iron(III), because this reagent gives relatively strong coloration with these ions in weakly acidic solution. In both cases, the full color developments occurred instantaneously at room temperature and the molar absorptivities of the complexes are of the order of  $10^4$ . In the case of iron(III), the value is  $1.54 \times 10^4$ . This value of the molar absorptivity is lower than the case of 2,4,6-*tri*-2-pyridyl-1,3,5-triazine,<sup>3)</sup> but higher than the case of 1,10-phenanthroline,<sup>4)</sup> 4,7-dihydroxy-1,10-phenanthroline,<sup>5)</sup> and 2,2'-bipyridine.<sup>4)</sup> This means that SSXB is useful as the spectrophotometric reagent for the determination of iron(III). Furthermore, it was found that this reagent reacts with iron(III) in the presence of cationic surface active agent, cetylpyridinium bromide (CPB), increasing the molar absorptivity about 20% of that in the absence of CPB, and that this coloration is also available with the photometric determination of iron(III).

This paper describes the color reactions of SSXB with some metal ions and the fundamental conditions for the spectrophotometric determinations of iron(III) in the absence of CPB and in the presence of CPB.

## Experimental

### Apparatus

A Hitachi-Perkin-Elmer model 139 spectrophotometer with 1 cm glass cells was used for the absorbance measurements, and a Hitachi-Horiba model M-5 glass electrode pH meter for the pH measurements.

### Reagents

**SSXB Solution** : A 0.1% SSXB solution was prepared by dissolving in distilled water a weighed amount of SSXB. The SSXB was synthesized by the Mannich condensation.<sup>1)</sup> One gram ( $2.4 \times 10^{-3}$  mol) of Paraxylenol Blue,  $2.4 \times 10^{-3}$  mol of sarcosine, and 0.5 g of sodium hydroxide were dissolved in 50 cm<sup>3</sup> of distilled water. After the water was distilled off, the mixture was dissolved in 40 cm<sup>3</sup> glacial acetic acid followed by adding 1 cm<sup>3</sup> of 37% formaldehyde and was kept at 45°C for 90 minutes with stirring. The solvent was, then, distilled off under reduced pressure. The SSXB was separated from the reaction mixture on a cellulose column by 1-butanol saturated with 0.1% acetic acid, which was the most suitable eluent among examined ones to separate the SSXB from other materials. The *R<sub>f</sub>* values of sarcosine, Paraxylenol Blue (PXB), SSXB, and Sarcosinexylenol Blue (SXB), 3,3'-bis[N-(carboxymethyl) methylaminomethyl]-*p*-xylenolsulfophthalein, were shown in Table 1, which were obtained from the examinations of a few kinds of eluents. The SSXB obtained was passed through a column of strongly acidic ion-exchange resin, Duolite C-20, to make it the free acid form, and

Table 1. Paper chromatography of reaction mixture

No.	Developer	Sarcosine Rf	SXB Rf	SSXB Rf	PXB Rf
1	1-butanol saturated with 0.1% acetic acid	0-0.03	0.03-0.07	0.13-0.37	0.59-0.93
2	1-butanol saturated with 1% acetic acid	0-0.03	0.03-0.08	0.12-0.36	0.71-0.92
3	1-butanol saturated with 5% acetic acid	0.02-0.06	0.05-0.09	0.16-0.34	0.82-0.96
4	1-butanol saturated with 10% acetic acid	0.03-0.1	0.09-0.13	0.16-0.42	0.85-0.94
5	1-butanol saturated with 0.1% acetic acid	0-0.04*	0.06-0.32*		
6	1-butanol saturated with 10% acetic acid	0.03-0.09*	0.12-0.36*		

SSXB=Semisarcosinexylenol Blue (This is a monosubstituted derivative of Paraxylenol Blue, while SXB is a disubstituted derivative.). PXB=Paraxylenol Blue.

\*Samples in the free acid form.

finally, SSXB in the free acid form was again chromatographed to remove sarcosine completely using 1-butanol saturated with 10% acetic acid as the eluent. The SSXB obtained as the orange compound had m.p. 145-147°C. The purity of this compound was checked by the paper chromatography, and it was confirmed that the compound gave only one spot. The result of the elemental analysis was as follows. Found : C, 59.14% ; H, 5.56% ; N, 2.63%. Calcd for  $C_{27}H_{29}O_7NS \cdot H_2O$  : C, 61.25% ; H, 5.86% ; N, 2.65%.

*Standard Iron(III) Solution* : A solution containing about  $1 \text{ mg cm}^{-3}$  of iron(III) was prepared by dissolving guaranteed reagent grade iron(III) nitrate in a small amount of nitric acid and diluting with distilled water. The solution was standardized by the complexometric back-titration with a standard solution of thorium using Xylenol Orange as an indicator. This solution was diluted as required.

*Standard Copper Solution* : A solution containing about  $1 \text{ mg cm}^{-3}$  of copper was prepared by dissolving copper nitrate trihydrate in a small amount of nitric acid and diluting with distilled water. The solution was standardized by complexometric titration with murexide as an indicator and diluted as required.

*Cationic Surface Active Agent Solutions* :  $0.01 \text{ mol dm}^{-3}$  solutions of each of cetyltrimethylammonium bromide (CTMAB), cetyltrimethylammonium chloride (CTMAC), cetylpyridinium chloride (CPC), and CPB were prepared by dissolving in 20% ethanol a weighed amount of these agents (Nakarai Chemicals).

*Buffer Solution* : The pH was adjusted with  $1 \text{ mol dm}^{-3}$  acetic acid- $1 \text{ mol dm}^{-3}$  sodium acetate,  $1 \text{ mol dm}^{-3}$  nitric acid -  $1 \text{ mol dm}^{-3}$  hexamine, and  $1 \text{ mol dm}^{-3}$  ammonium chloride- $1 \text{ mol dm}^{-3}$  aqueous ammonia.

All the other reagents used were of guaranteed reagent grade.

## Recommended Procedures

*Procedure in the Absence of CPB* : A sample solution containing up to  $35 \mu\text{g}$  of iron(III) is

taken into 25 cm<sup>3</sup> volumetric flask. Then, 2 cm<sup>3</sup> of 0.1% SSXB solution and 10 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> nitric acid–1 mol dm<sup>-3</sup> hexamine buffer solution are added. After making up the volume to 25 cm<sup>3</sup> (the final pH : 6.0), the absorbance is measured at 528 nm against a reagent blank as a reference.

*Procedure in the Presence of CPB* : A sample solution containing up to 35 μg of iron(III) is taken into 25 cm<sup>3</sup> volumetric flask. Then, 2 cm<sup>3</sup> of 0.1% SSXB solution, 10 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> acetic acid –1 mol dm<sup>-3</sup> sodium acetate buffer solution, and 1 cm<sup>3</sup> of 0.01 mol dm<sup>-3</sup> CPB are added. After making up the volume to 25 cm<sup>3</sup> (the final pH : 5.0), the absorbance is measured at 540 nm against a reagent blank as a reference.

## Results and Discussion

### Absorption Curves of SSXB

The absorption spectra of 16 μg cm<sup>-3</sup> SSXB solution in various pH are shown in Fig. 1. The SSXB solution colors reddish-orange in 3 mol dm<sup>-3</sup> hydrochloric acid. The color of the solution changes to yellow with increase in pH, but over the pH range from about 2 to 6.0, there is no color change and the solutions show the almost same absorption curves which have an absorption maximum at 450–453 nm. By further increase of pH value, however, the color of the solution changes again, and it becomes yellow-green at pH 7.0, and violet at pH 9–11. According to these color changes, the absorption maximum of 450–453 nm decreases, accompanied with the increase of that of 590–593 nm.

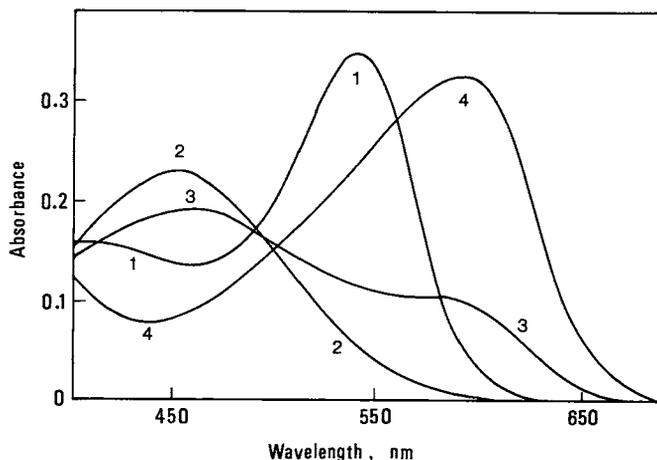


Fig. 1. Absorption spectra of SSXB in a 25 cm<sup>3</sup> aqueous solution containing 2 cm<sup>3</sup> of 0.02% SSXB solution at 3 mol dm<sup>-3</sup> hydrochloric acid media (1), pH 6 (2), pH 7 (3), or pH 10 (4). The absorbances were measured against water as a reference.

### Complexes of SSXB and Metal Ions

The color reactions between SSXB and metal ions were investigated. The metal ions

which gave colors are summarized in Table 2. Indium, lead, copper, zinc, scandium, zirconium, thorium, iron(III), cobalt, and nickel forms colored complexes with SSXB, but these colors except copper and iron(III) complexes are weak. Copper and iron(III) gave relatively strong colors whose molar absorptivities are  $1.38 \times 10^4$  and  $1.54 \times 10^4$ , respectively, and these colorations are available to the spectrophotometric determinations of these ions.

Table 2. Reactions of SSXB with metal ions

Ion	pH	Color of Complex
In <sup>3+</sup>	6-8	Reddish-yellow
Pb <sup>2+</sup>	9-11	Reddish-violet
Cu <sup>2+</sup>	5-8	Reddish-violet
Zn <sup>2+</sup>	8-10	Reddish-violet
Sc <sup>3+</sup>	6-7	Orange-red
Zr <sup>4+</sup>	2-3	Red
Th <sup>4+</sup>	7-8	Reddish-violet
Fe <sup>3+</sup>	6-8	Reddish-violet
Co <sup>2+</sup>	6-7	Orange-red
Ni <sup>2+</sup>	10-11	Blue-violet

### Absorption Curves of Iron(III) Complex

The absorption spectra of the iron(III) complex obtained by the recommended procedures are shown in Fig. 2. The colored solution of the iron(III) complex in the absence of CPB has an absorption maximum at 526-529 nm at pH value of 6.0 and the peak of the spectrum is not shifted by the pH change within the range from pH 5.0 to 6.5. In the presence of CPB, the colored solution of the iron(III) complex shows the maximum absorption at 540-542 nm.

### The Effect of pH

The effect of pH on the color development of the solution containing 30  $\mu\text{g}$  of iron(III) was examined with both cases in the absence and in the presence of CPB by measuring the absorbances of colored mixtures at 528 nm and 540 nm, respectively. As the results are shown

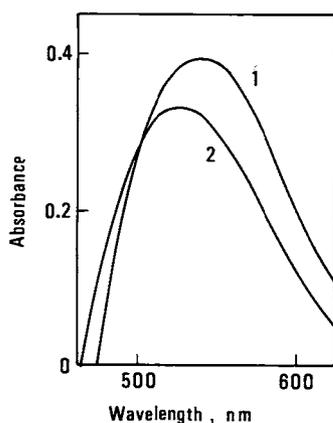


Fig. 2. Absorption spectra of Iron(III)-SSXB complexes in a 25 cm<sup>3</sup> aqueous solution containing 30  $\mu\text{g}$  of iron(III) and 2 cm<sup>3</sup> of 0.1% SSXB solution in the presence of 1 cm<sup>3</sup> of 0.01 mol dm<sup>-3</sup> CPB solution at pH 5.0 (1) or in the absence of it at pH 6.0 (2). The absorbances were measured against reagent blanks as references.

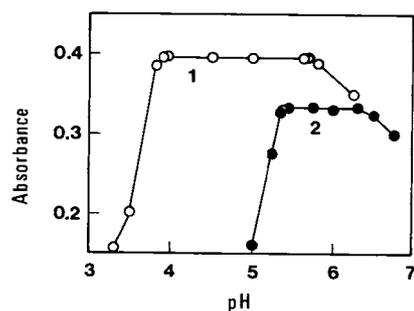


Fig. 3. The effect of pH on the absorbances of iron(III)-SSXB complexes with a 25 cm<sup>3</sup> of solution containing 30  $\mu\text{g}$  of iron(III) and 2 cm<sup>3</sup> of 0.1% SSXB solution in the presence of 1 cm<sup>3</sup> of 0.01 mol dm<sup>-3</sup> CPB solution (1) or in the absence of it (2). The absorbances were measured at 540 nm (1) and 528 nm (2) against reagent blanks as references.

in Fig. 3, the ranges in which the maximum and nearly constant absorbances are obtained are pH 5.4–6.3 in the absence of CPB and pH 3.9–5.7 in the presence of it.

### The Effect of the Amount of SSXB

The effect of the reagent concentration on the color development was studied with the solutions containing 30  $\mu\text{g}$  of iron(III) and various amounts of 0.1% SSXB solution. The results are shown in Fig. 4. The maximum and almost constant absorbances were obtained by adding from 2–4  $\text{cm}^3$  of SSXB solution in absence of CPB and from 2–5  $\text{cm}^3$  in the presence of CPB.

### The Effect of the Amount of the Buffer Solution

The effect of the amount of 1  $\text{mol dm}^{-3}$  nitric acid – 1  $\text{mol dm}^{-3}$  hexamine or 1  $\text{mol dm}^{-3}$  acetic acid – 1  $\text{mol dm}^{-3}$  sodium acetate buffer solution on iron(III) complex was examined in the absence of CPB or in the presence of it, respectively. The results indicated that the addition from 5 to 15  $\text{cm}^3$  of the buffer solution has no effect on the color intensity of the iron(III) complex in either case.

### The Effect of the Amount of CPB

Various amounts of 0.01  $\text{mol dm}^{-3}$  CPB solution were added to a solution containing 30  $\mu\text{g}$  of iron(III) and 2  $\text{cm}^3$  of 0.1% SSXB solution, and the absorbances were measured at 540 nm according to the recommended procedure for the presence of CPB. The absorbance of the colored solution was increased with increasing the adding amounts of CPB, and the maximum absorption wavelength was sifted toward a longer wavelength. As the results are shown in Fig. 5, however, the maximum and nearly constant absorbances were obtained at 540–542 nm by adding from 0.5 to 5  $\text{cm}^3$  of CPB solution. On the other hand, when CTMAC, CTMAB, or CPC was used instead of CPB, the absorbance of complex became lower than the case of CPB.

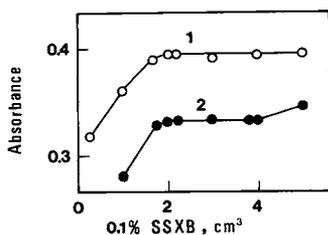


Fig. 4. Effect of SSXB concentration on the absorbance of iron(III)-SSXB complex examined with a 25  $\text{cm}^3$  solution containing 30  $\mu\text{g}$  of iron(III) in the presence of 1  $\text{cm}^3$  of 0.01  $\text{mol dm}^{-3}$  CPB solution at pH 5.0 (1) or in the absence of it at pH 6.0. The absorbances were measured at 540 nm (1) and 528 nm (2) against reagent blanks as references.

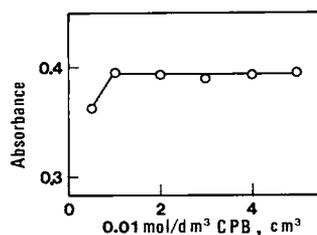


Fig. 5. Effect of CPB concentration on the absorbance of iron(III)-SSXB complex examined with a 25  $\text{cm}^3$  solution containing 30  $\mu\text{g}$  of iron and 2  $\text{cm}^3$  of 0.1% SSXB solution at pH 5.0. The absorbances were measured at 540 nm against reagent blanks as references.

One  $\text{cm}^3$  of  $0.01 \text{ mol dm}^{-3}$  CPB solution was therefore used in further experiments.

### The Stability of the Color

The color development for the iron(III) complex occurs instantaneously at room temperature, and the color intensity was not affected with heating in  $30\text{--}90^\circ\text{C}$  water bath for at least 15 minutes. The color, once developed, was very stable, and the absorbance remained almost constant for at least three hours, either in the absence of CPB or in the presence of it.

### Calibration Curves

The calibration curves for iron(III) which were prepared by the recommended procedures are shown in Fig. 6. In the absence of CPB, Beer's law is obeyed up to  $1.4 \mu\text{g cm}^{-3}$  of iron(III). The molar absorptivity of the complex calculated from the curve and the sensitivity of the determination are  $1.54 \times 10^4$  and  $3.7 \times 10^{-3} \mu\text{g cm}^{-2}$  of iron(III) for  $\log(I_0/I) = 0.001$ , respectively. When this molar absorptivity of the complex is compared with those of other reagents, it's sensitivity is lower than that of the 2,4,6-tri-2-pyridyl-1,3,5-triazine (molar absorptivity,  $\epsilon = 2.23 \times 10^4$ ).<sup>3)</sup> However, it is higher than 1,10-phenanthroline ( $\epsilon = 1.1 \times 10^4$ ),<sup>4)</sup> 4,7-dihydroxy-1,10-phenanthroline ( $\epsilon = 1.5 \times 10^4$ ),<sup>5)</sup> and 2,2'-bipyridine ( $\epsilon = 8.3 \times 10^3$ ).<sup>4)</sup> In the presence of CPB, linear relationship between the absorbance and the concentration holds up to  $1.4 \mu\text{g cm}^{-3}$  of iron(III). The molar extinction coefficient and the sensitivity according to Sandell's expression are  $1.84 \times 10^4$  and  $3.0 \times 10^{-3} \mu\text{g cm}^{-2}$  of iron(III), respectively. The reproducibilities of the methods, expressed by the relative standard deviations of the absorbances which were obtained from five repeat determinations, were 1.51% for the method of the absence of CPB and 1.64% for that of the presence of it.

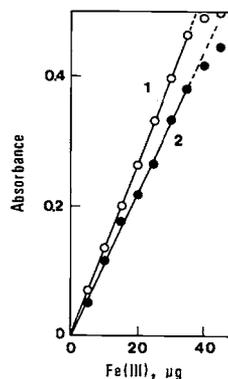


Fig. 6. Calibration curves of iron(III) in a  $25 \text{ cm}^3$  aqueous solution containing  $2 \text{ cm}^3$  of  $0.1\%$  SSXB solution in the presence of  $1 \text{ cm}^3$  of  $0.01 \text{ mol dm}^{-3}$  CPB solution at pH 5.0 (1) or in the absence of it at pH 6.0. The absorbances were measured at  $540 \text{ nm}$  (1) and  $528 \text{ nm}$  (2) against reagent blanks as references.

### The Effect of Diverse Ions

According to the recommended procedure, the effect of 24 diverse ions on the determination of  $30 \mu\text{g}$  of iron(III) in the absence of CPB was examined. The results obtained are summarized in Table 3. Iron(III) can be determined within 5% errors in the presence of 1 mg each of alkali metals, alkaline earth metals, aluminum, vanadium(V), molybdenum(VI), manganese(II), and platinum(IV),  $500 \mu\text{g}$  each of cadmium and yttrium,  $100 \mu\text{g}$  each of lead, zinc, thorium, chromium(III), and fluoride, and  $30 \mu\text{g}$  each of indium and scandium. Copper, zirconium, tungsten(VI), cobalt, nickel, and tartrate interfere with the determination, but the

effect of cobalt is eliminated by the addition of 2 cm<sup>3</sup> of 1% hydrogen peroxide. The influence from copper is also eliminated by the separation of ammine complex of copper from iron(III) hydroxide which are formed by the addition of aqueous ammonia to the solution containing iron(III) and copper.

Table 3. Effect of diverse ions on the determination of iron(III)

Ion	Amount added ( $\mu\text{g}$ )	Iron(III) found ( $\mu\text{g}$ )	Ion	Amount added ( $\mu\text{g}$ )	Iron(III) found ( $\mu\text{g}$ )
Li <sup>+</sup>	1,000	29.9	Th <sup>4+</sup>	100	28.9
K <sup>+</sup>	1,000	30.2	Cr <sup>3+</sup>	100	31.1
Mg <sup>2+</sup>	1,000	30.2	In <sup>3+</sup>	30	31.0
Ca <sup>2+</sup>	1,000	30.4	Sc <sup>3+</sup>	30	31.2
Al <sup>3+</sup>	1,000	30.0	Cu <sup>2+</sup>	30	33.5
V(V)	1,000	29.8	" a)	1,000	30.0
Mo(VI)	1,000	30.3	Zr <sup>4+</sup>	30	26.2
Mn <sup>2+</sup>	1,000	29.0	W(VI)	30	27.6
Pt(IV)	1,000	29.8	Co <sup>2+</sup>	30	35.2
Cd <sup>2+</sup>	500	30.0	" b)	100	31.0
Y <sup>3+</sup>	500	30.0	Ni <sup>2+</sup>	30	33.2
Pb <sup>2+</sup>	100	28.8	F <sup>-</sup>	100	30.1
Zn <sup>2+</sup>	100	28.7	Tartrate	1,000	28.0

Thirty micrograms of iron(III) was taken.

a) Three cm<sup>3</sup> of 1 mol dm<sup>-3</sup> aqueous ammonia was added. Then iron(III) was separated as iron(III) hydroxide from the ammine complex of copper by filtration.

b) Two cm<sup>3</sup> of 1% hydrogen peroxide was added.

### The Composition of the Complexes

The composition of the iron(III)-SSXB complex in the absence of CPB was examined at pH

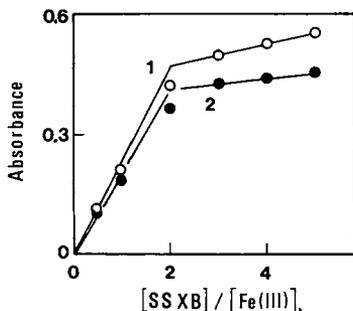


Fig. 7. The mole ratio method examined with 25 cm<sup>3</sup> solutions containing a constant amount of iron(III),  $9.0 \times 10^{-7}$  mol, and various amounts of SSXB at pH 6.0. The absorbances were measured at 528 nm (1) and 560 nm (2) against reagent blanks as references.

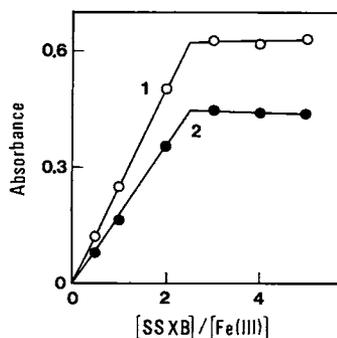


Fig. 8. The mole ratio method examined with 25 cm<sup>3</sup> solutions containing a constant amount of iron(III),  $9.0 \times 10^{-7}$  mol, and various amounts of SSXB in the presence of 1 cm<sup>3</sup> of 0.01 mol dm<sup>-3</sup> CPB solution at pH 5.0. The absorbances were measured at 540 nm (1) and 500 nm (2) against reagent blanks as references.

6.0 by the mole ratio method, measuring the absorbance at the wavelengths, 528 and 560 nm. In this experiment, various amounts of SSXB were added to a constant amount of iron(III),  $9.0 \times 10^{-7}$  mol. As the results are shown in Fig. 7, the equivalence points in the mole ratio method indicated the formation of a 1 : 2 iron(III)-SSXB complex at both 528 and 560 nm. Then, the composition of the iron(III)-SSXB complex in the presence of CPB was examined at pH 5.0 by the mole ratio method, measuring the absorbances at the wavelengths, 500 and 540 nm. In the presence of  $1 \text{ cm}^3$  of  $0.01 \text{ mol dm}^{-3}$  CPB, this time, various amounts of SSXB were added to a constant amount of iron(III),  $9.0 \times 10^{-7}$  mol. As the results are shown in Fig. 8, the equivalence points indicated that iron(III) forms 1 : 2.5 complex with SSXB. Next, the mole ratio of CPB combined with Fe(III)(SSXB)<sub>2.5</sub> complex was investigated at pH 5.0 by the mole ratio method, measuring the absorbance at the wavelengths, 500 and 540 nm. In this experiment, various amounts of CPB were added to a constant amount of Fe(III)(SSXB)<sub>2.5</sub> complex,  $9.0 \times 10^{-7}$  mol. As the results are shown in Fig. 9, it seems that Fe(III)(SSXB)<sub>2.5</sub> complex and CPB formed 1 : 4 complex. From these results, the mole ratio of iron(III), SSXB, and CPB is estimated to be 2 : 5 : 8.

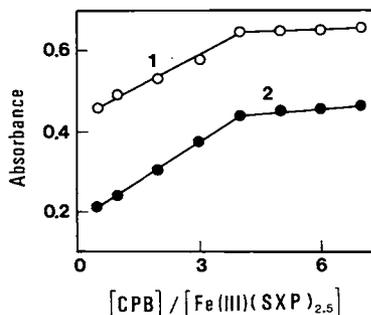


Fig. 9. The mole ratio method examined with  $25 \text{ cm}^3$  solutions containing a constant amount of Fe(III)(SSXB)<sub>2.5</sub> complex,  $9.0 \times 10^{-7}$  mol, and various amounts of CPB at pH 5.0. The absorbances were measured at 540 nm (1) and 500 nm (2) against reagent blanks as references.

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