

2-(2-THIAZOLYLAZO)-4-METHYL-5-(SULFOMETHYLAMINO)BENZOIC ACID  
AS METALLOCHROMIC INDICATOR FOR NICKEL

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Some thiazolylazo- and pyridylazobenzoic acids were studied for the metallochromic indicator in EDTA titration of nickel: 2-(2-thiazolylazo)-4-methyl-5-(sulfomethylamino)benzoic acid (TAMSMB), 2-(5-bromo-2-thiazolylazo)-4-methyl-5-(sulfomethylamino)benzoic acid (5-Br-TAMSMB), 2-(2-thiazolylazo)-5-(N-ethyl-N-sulfomethylamino)benzoic acid (N-Et-TASMB) and 2-(3,5-dichloro-2-pyridylazo)-4-methyl-5-(sulfopropylamino)benzoic acid (3,5-diCl-PAMSPB). The formation constants of the nickel chelates with these reagents and the rate of the substitution reaction of nickel-TAMSMB chelate with EDTA were determined. TAMSMB is an excellent indicator for nickel because of the good color contrast between indicator and the nickel chelate, the large rate of color change reaction at equivalence point and the easy preparation of the reagent.

INTRODUCTION

In chelatometric titrations, the color change of the indicator near the equivalence point is governed by the rate of the substitution reaction between the metal indicator chelate and the titrant, as well as by the equilibrium involved.

Some pyridylazo- and thiazolylazophenols have been recommended for the metallochromic indicators in the EDTA titrations of nickel<sup>1)-4)</sup>. These indicators form the  $ML_2$  chelates with nickel and satisfy the equilibrium demand, while the rate of the color change reaction is usually slow; titrations should be carried out at about 80°C or higher.

In a previous study<sup>5)</sup>, it was found that thiazolylazobenzoic acid derivatives such as 2-(2-thiazolylazo)-5-(dimethylamino)benzoic acid (TAMB) and 2-(2-thiazolylazo)-5-(sulfomethylamino)benzoic acid (TASMB) mainly form the 1 : 1 chelate with nickel in contrast to thiazolylazo- and pyridylazophenols, and the possibility of their application to the metallochromic indicator for nickel was suggested. TAMB and its nickel chelate are not so soluble in water and also the preparation and the purification of TASMB are troublesome. In this study, 2-(2-thiazolylazo)-4-methyl-5-(sulfomethylamino)benzoic acid (TAMSMB), 2-(5-bromo-2-thiazolylazo)-4-methyl-5-(sulfomethylamino)benzoic acid (5-Br-TAMSMB), 2-(2-

thiazolylazo)-5-(N-ethyl-N-sulfomethylamino)benzoic acid(N-Et-TASMB) and 2-(3,5-dichloro-2-pyridylazo)-4-methyl-5-(sulfopropylamino)benzoic acid(3,5-diCl-PAMSPB) were examined, and the mechanism of color change reaction of TAMSMB near the equivalence point was discussed.

## EXPERIMENTAL

### Preparation of reagents

TAMSMB and 5-Br-TAMSMB were prepared by the method described in the previous paper<sup>6)</sup>.

N-Et-TASMB. 3-(Ethylamino)benzoic acid was prepared from ethyliodide and 3-aminobenzoic acid<sup>7)</sup>. After being recrystallized from the mixture of ethanol and water, the product was methylsulfonated and coupled with diazotized 2-aminothiazole by similar procedure to that for TAMSMB. The purification was done as previously<sup>6)</sup>. Elemental analysis(m.p. 250°C dec.): calcd. for  $C_{13}H_{14}N_4O_5S_2 \cdot 2H_2O$ , 38.4%C, 4.5%H, 13.8%N; found, 38.7%C, 4.3%H, 13.9%N.

3,5-diCl-PAMSPB. 3-Amino-4-methylbenzoic acid(0.02 mol) and propanesultone(0.02 mol) were added to n-butanol(50 ml), and the mixture was heated on a steam bath for 3 h. The yellow precipitate of 3-sulfopropylamino-4-methylbenzoic acid obtained and the diazonium compound prepared from 2-amino-3,5-dichloropyridine as usual were added to ethanol(50 ml), the solution was stirred, and carbon dioxide was bubbled through it for 15 min. After the solution was filtered, the filtrate was allowed to stand overnight in a refrigerator. The red precipitate was obtained and washed with methanol. Elemental analysis(m.p. 205°C dec.): calcd. for  $C_{16}H_{14}N_4O_5S_2Cl_2Na_2$ , 39.1%C, 2.9%H, 11.4%N; found, 38.8%C, 2.8%H, 10.6%N.

### Reagents and apparatus

TAMSMB, 5-Br-TAMSMB, and N-Et-TASMB were dissolved in 0.1M acetate buffer (pH 5 - 6), and 3,5-diCl-PAMSPB in water( $5 \times 10^{-4}M$ ).

A standard solution of nickel( $10^{-2}M$ ) was prepared from nickel sponge(purity 99.99%). A standard solution of EDTA( $10^{-2}M$ ) was prepared from  $Na_2H_2edta$  and standardized against a standard zinc(II) solution with xylenol orange as indicator.

Buffer solution. Acetic acid-acetate solution(1M, pH 3 - 7) or 2-morpholino-1-ethanesulfonic acid(MES)-potassium hydroxide solution(pH 4 - 6) was used.

All water used had been redistilled from a hard glass vessel.

A Union Giken Model SM-401 spectrophotometer, a Union Giken Model RA-401 stopped flow spectrophotometer, a Hirma automatic titrator, and a Radiometer Model PHM 26 pH meter were used.

## RESULTS AND DISCUSSION

### Acidity constants of the reagents

Acidity constants obtained as previously<sup>6)</sup> are given in Table 1 together with those of TASMB and TAMB.

### Composition and formation constants of nickel chelate

The absorption spectra of nickel chelates with these reagents are shown in Fig. 1 and Fig. 3. The molar absorptivities of nickel chelates(NiL) with TAMSMB,

Table 1 Acidity constants of the reagents and formation constants of the nickel chelates( $\mu = 0.1$ , 25°C)

| Reagent         | $pK_{NH}$         | $pK_{COOH}$      | $\log K_{NiL}$   | $\log K_{NiL_2}$ |
|-----------------|-------------------|------------------|------------------|------------------|
| TAMSMB          | 1.3 <sup>a</sup>  | 3.4 <sup>a</sup> | 5.3              | 3.9              |
| 5-Br-TAMSMB     | <0.5 <sup>a</sup> | 3.1 <sup>a</sup> | 4.1              | -                |
| N-Et-TASMB      | 1.4               | 3.3              | 5.2              | -                |
| 3,5-diCl-PAMSPB | <0.5              | 4.1              | 6.5              | 5.3              |
| TAMB            | 1.9 <sup>b</sup>  | 3.6 <sup>b</sup> | 5.5 <sup>c</sup> | -                |
| TASMB           | 1.3 <sup>a</sup>  | 3.3 <sup>a</sup> | 4.8              | -                |

a: reference 6, b: reference 5, c: in 2%(v/v) dioxane,  
-: not determined.

5-Br-TAMSMB, N-Et-TASMB and 3,5-diCl-PAMSPB were 45000, 39000, 47000 and 60000  $l\ mol^{-1}\ cm^{-1}$  at the maximum absorption wavelength, respectively.

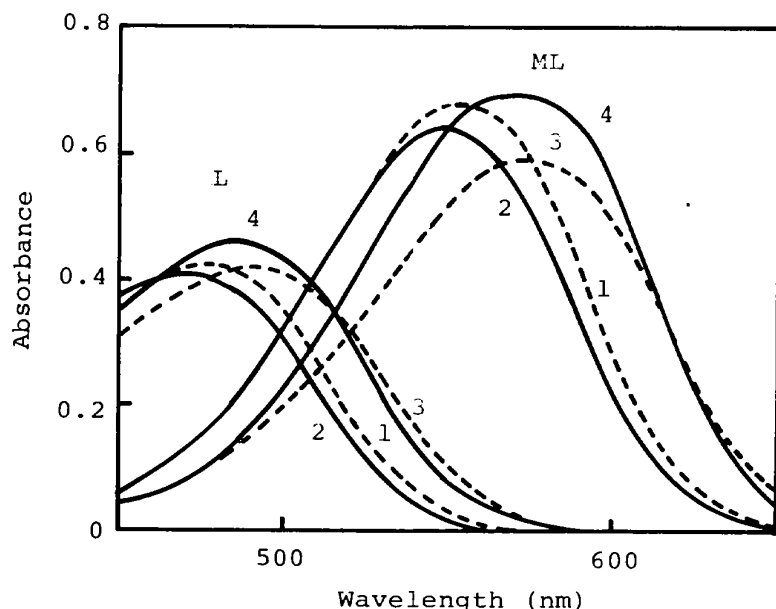


Fig. 1 Absorption spectra of reagents(L) and the nickel chelates(ML) at pH 5.0

$$C_L = 1.50 \times 10^{-5} M$$

$$C_{Ni} = 6.20 \times 10^{-4} M$$

(1) TAMSMB; (2) TASMB;

(3) 5-Br-TAMSMB;

(4) N-Et-TASMB

The results of Job's method(Fig. 2), the molar ratio method and the absorption spectra of the nickel chelate clearly showed that TAMSMB, 5-Br-TAMSMB and N-Et-TASMB as well as TAMB or TASMB form 1 : 1 chelate with nickel, unless the concentration of the reagent is not so high. However, in the case of 3,5-diCl-PAMSPB, the absorption spectra of the nickel chelates gave the isosbestic points at 530 nm and 494 nm(Fig. 3), which indicate the formation of both  $NiL$  and  $NiL_2$  chelates in contrast to those with TAMSMB which gave only one isosbestic point at 502 nm. The formation constants of nickel chelates( $K_{NiL} = [NiL]/[Ni][L]$  and  $K_{NiL_2} = [NiL_2]/[NiL][L]$ ) were determined by spectrophotometry. The results are given in Table 1. From these formation constants these reagents are expected to give the sharp color change in EDTA titrations of nickel from the equilibrium point of view.

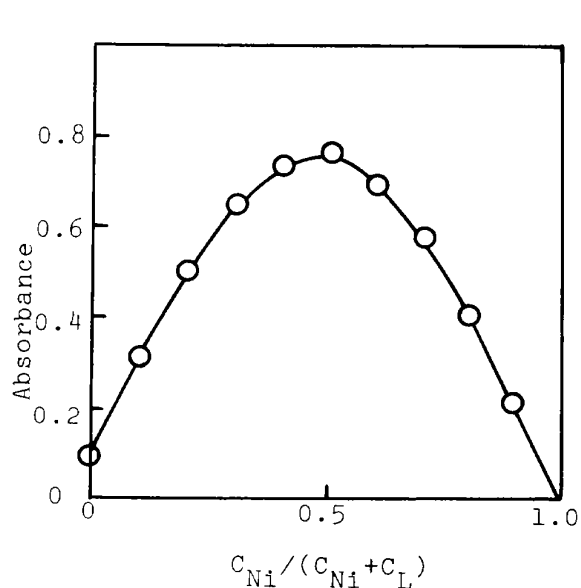


Fig. 2 Composition of Nickel-TAMSMB chelate

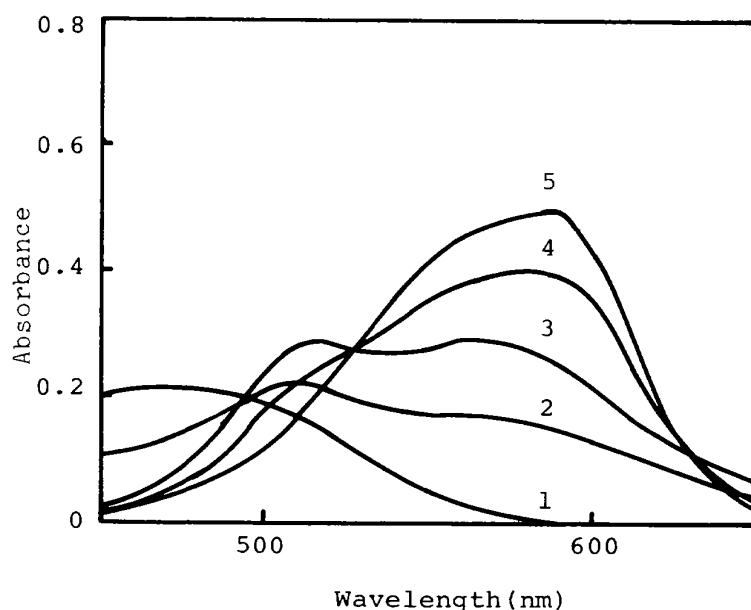


Fig. 3 Absorption spectra of 3,5-diCl-PAMSPB and the nickel chelates at pH 5.3

$C_L = 8.40 \times 10^{-6} M$ ,  $C_{Ni} =$  (1) none; (2)  $2.07 \times 10^{-6} M$ ; (3)  $4.14 \times 10^{-6} M$ ; (4)  $8.27 \times 10^{-6} M$ ; (5)  $2.07 \times 10^{-4} M$

#### Photometric titration of nickel

The sharpness of the indicator color change at equivalence point was examined by photometric titration. A  $10^{-3} M$  nickel solution was titrated with a 0.01M EDTA solution using TAMSMB, N-Et-TASMB or TASMB as an indicator at 40°C and with 3,5-diCl-PAMSPB at 80°C. As can be seen in Fig. 4, TAMSMB, N-Et-TASMB or TASMB gave accurate results if titrated to the complete color change at pH 4-6.5. With 3,5-diCl-PAMSPB, however, the color change was sluggish, because the rate of the ligand substitution on the chelate was very slow.

#### Visual titration of nickel

An aliquot of  $10^{-2} M$  nickel solution was diluted to about 50 ml with water and 2 - 3 ml of 1M acetic acid -acetate buffer and 0.2 - 0.5 ml of indicator solution ( $5 \times 10^{-4} M$ ) were added. The solution was heated to 40 - 50°C, and titrated with  $10^{-2} M$  EDTA solution. The end point from purple to yellow with TAMSMB, from violet to orange with 5-Br-TAMSMB or N-Et-TASMB was obtained. In the case of TAMSMB the contrast of the color change was better than that of 5-Br-TAMSMB or N-Et-TASMB. With 3,5-diCl-PAMSPB the titration should be done at a boiling temperature. Both TAMSMB and TASMB are good indicators for visual titration, but the synthesis and the purification of TAMSMB are much easier, and TAMSMB is now commercially available from Dojin Lab. Co., Kumamoto.

Trace amount of cobalt did not block the color change of TAMSMB, since cobalt(III)-TAMSMB chelate forms slowly in the absence of oxidizing reagent.

The results are shown in Table 2.

Table 2 Visual EDTA-titrations of nickel with TAMSMB as indicator

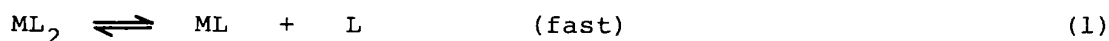
| pH  | Ni taken (mg) | Ni found (mg) |
|-----|---------------|---------------|
| 4.4 | 3.29          | 3.30          |
|     | 6.58          | 6.58          |
|     | 9.86          | 9.86          |
| 5.4 | 3.29          | 3.29          |
|     | 6.58          | 6.58          |
|     | 9.86          | 9.86          |
| 6.0 | 1.39          | 1.37          |
|     | 2.78          | 2.78          |
|     | 5.56          | 5.55          |
|     | 9.86          | 9.86          |

Mechanism of the substitution reaction of nickel-TAMSMB chelate with EDTA

The rate of the substitution reaction of the TAMSMB chelate with EDTA was measured. A solution containing nickel[(0.780 - 1.515)  $\times 10^{-5}$  M], TAMSMB [(1.016 - 3.385)  $\times 10^{-5}$  M], a MES-potassium hydroxide buffer(0.01M), potassium nitrate(0.1M) and a solution containing EDTA[(0.234 - 4.09)  $\times 10^{-3}$  M], a MES-potassium hydroxide buffer(0.01M), potassium nitrate(0.1M) were mixed at 25°C, and the decrease in the absorbance at 554 nm was recorded as a function of the reaction time on the stopped flow spectrophotometer. The rate law was expressed as  $-d[\text{NiL}]/dt = k_{0(\text{L,EDTA,H})}[\text{NiL}]$ , where  $k_{0(\text{L,EDTA,H})}$  is the conditional rate constant involving the concentrations of TAMSMB, EDTA and hydrogen ion.

The values of  $k_{0(\text{L,EDTA,H})}$  were proportional to the EDTA concentration and increased with increasing pH above 4.5, but were independent of the concentration of TAMSMB. The rate law can be written as  $-d[(\text{NiL})']/dt = k_{0(\text{H})}[(\text{NiL})'][\text{edta}']$ , where  $[(\text{NiL})']$  and  $[\text{edta}']$  denote the total concentrations of 1 : 1 nickel-TAMSMB chelates and of EDTA not combined with nickel ion, respectively.

When indicator forms  $\text{ML}_2$  chelate, the color change reaction proceeds as



that is, ML at equilibrium with  $\text{ML}_2$  undergoes the ligand substitution with EDTA,

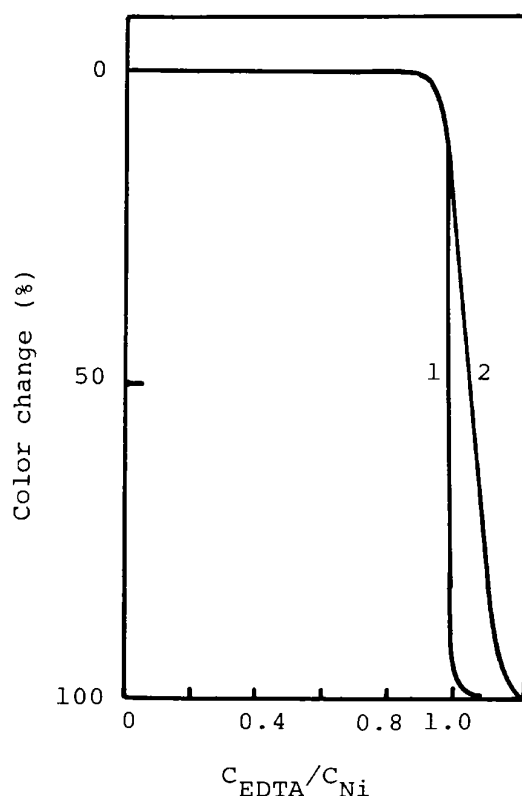


Fig. 4 Photometric titration curve of nickel with EDTA at pH 4 - 6.5

$C_{\text{Ni}} = 10^{-3}$  M: (1) TAMSMB, N-Et-TASMB, or TASMB at 40°C with a 562 nm filter  
(2) 3,5-diCl-PAMSPB at 80°C with a 575 nm filter

$C_{\text{Ind}} = 5 \times 10^{-6}$  M

Titration speed: 0.7 ml/min

and the rate law is expressed as<sup>8)-11)</sup>

$$-\frac{d[ML_2]}{dt} = k \frac{[ML_2][edta']}{K_{ML_2}[L]} \quad (3)$$

Therefore, in the case of TAMSMB only NiL chelate participated in the indicator color change reaction.

A plot of  $k_{0(H)}$  vs. pH is shown in Fig. 5. The increase in  $k_{0(H)}$  value with pH may be attributed to the fast substitution reaction of NiL(OH) chelate in the pH range higher than 4.5, because in the substitution reactions of copper(II)-1-(2-pyridylazo)-2-naphthol (PAN)<sup>10)</sup>, nickel-2-(2-pyridylazo)-4-methylphenol(PAC) and the other nickel chelates<sup>9)11)</sup> with EDTA, the difference in the rate of the substitution reaction

with different protonated forms of EDTA had not been observed, and in the substitution reaction of nickel-PAC and the other nickel chelates with EDTA NiL(OH) chelate was involved in the pH range higher than 5<sup>9)11)</sup>.

The rate constant of the nickel-TAMSMB chelate(NiL) for the reaction (2) was estimated as  $k = 22 \text{ M}^{-1}\text{s}^{-1}$  from the constant values of  $k_{0(H)}$  around pH 4. This value is comparable with that of nickel-PAC chelate( $k = 69 \text{ M}^{-1}\text{s}^{-1}$  in 20% dioxane)<sup>11)</sup>. However, PAC forms NiL<sub>2</sub> chelate, thus the overall rate of the substitution reaction of TAMSMB chelate is much faster than that of PAC chelate.

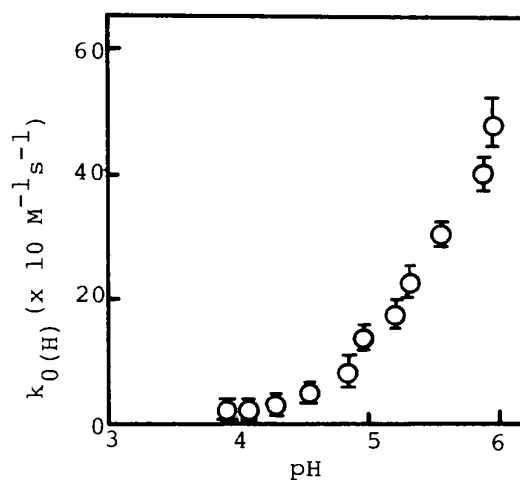


Fig. 5 Plot of  $k_{0(H)}$  vs. pH

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#### Keyword phrases

metallochromic indicator of nickel; 2-(2-thiazolylazo)-4-methyl-5-(sulfo-methylamino)benzoic acid; mechanism of ligand substitution reaction.

(Received Mar. 18, 1983)