Calmagite:[1] The Formation Constants of Zinc(II) Chelates and Its Use as a Metal Indicator

Genkichi NAKAGAWA, Hiroko WADA, and Yoshio FUJITA
Nagoya Institute of Technology, Showa-ku, Nagoya

(Received July 12, 1972)

The acid dissociation constants of Calmagite [1-(2-hydroxy-5-methylphenylazo)-2-naphthol-4-sulfonic acid] and the formation constants of zinc(II) chelates have been determined spectrophotometrically at 25°C and at the ionic strengths of 0.1 and 1.0. In an ammoniacal medium zinc forms mixed-ligand complexes with Calmagite (I^{3-}) and ammonia (X); $ZnIX_n^-$. The formation constants of the zinc(II)-Calmagite chelates are $\log K_{ZnI}=11.75$, $\log K_{ZnI_2}=7.82$, $\log K^{X}_{ZnIX}=2.09$, and $\log K^{X}_{ZnIX_2}=1.70$ ($\mu=1.0$). Calmagite is recommended as an indicator for the titration of zinc(II) with EDTA. The color transition of Calmagite is clearer and sharper, and the aqueous solution of the indicator is more stable, than in the case of Eriochrome Black T.

Eriochrome Black T has been exclusively used as a metal indicator in the complexometric titration of magnesium, zinc, cadmium, lead, etc. Lindstrom and Diehl recommended Calmagite as the metal indicator for magnesium,[2] because the aqueous solution of Calmagite is more stable than that of Eriochrome Black T. However, Calmagite has not been so much used for a metal indicator as Eriochrome Black T. Kodama and Miyamoto[3] determined the stability constants of Calmagite chelates of copper(II), nickel(II), cobalt(II), zinc(II), cadmium(II), and lead(II) by the exchange reaction of Calmagite with the metalnitrilotriacetic acid chelates and proposed the use of Calmagite as an indicator for zinc, cadmium, and lead. Their value of the stability constant of zinc-Calmagite seems, however, to be too high in comparison with that of the zinc-Eriochrome Black T chelate.

The present paper will deal with the formation of mixed-ligand complexes of zinc-Calmagite chelates in an ammoniacal medium and with the behavior of Calmagite as a metal indicator for zinc in detail.

Experimental

Reagents. *Zinc Chloride*: Zinc metal (99.999%) was dissolved in hydrochloric acid to prepare a zinc chloride solution.

Calmagite: Calmagite from the Dōjindō Co., Ltd., was purified by a procedure described by Lindstrom and Diehl.[2] The Calmagite stock solution was prepared every week and was standardized with a copper standard solution by photometric titration.

EDTA: Reagent-grade EDTA·2Na obtained from the Dōjindō Co., Ltd., was dissolved in distilled water and standardized complexometrically against a standard zinc solution.

Ammonia Solution: A reagent-grade ammonia solution was distilled, and pure ammonia was collected in distilled water. The concentration of ammonia was determined with a standard hydrochloric acid solution.

Potassium Acetate and Potassium Nitrate: Reagent-grade chemicals were purified by recrystallization.

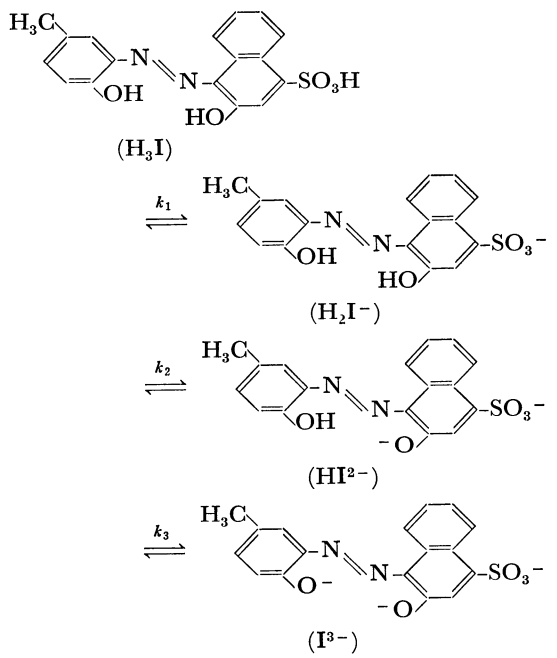
Acetic Acid, Boric Acid and Postassium Hydroxide: Reagent-grade chemicals were used without further purification.

Apparatus. A Hitachi Model 124 Double-beam Spectrophotometer, a Hitachi Model 356 Two-wavelength Double-beam Spectrophotometer, a Hitachi-Horiba pH Meter type F-5 equipped with Horiba glass and calomel electrodes, and a Hirama Automatic Recording Titrator were used.

Experimental Procedure. The ionic strength was maintained at 0.1 or 1.0 with potassium nitrate. The pH was adjusted by adding buffer solutions of potassium acetate-acetic acid, potassium hydroxide-boric acid, or ammonia-ammonium chloride. The absorbance of the solution was measured by the use of a silica cell with a light path of 1.0 cm. After measuring the absorbance, the accurate pH value was measured with a pH meter which had been calibrated with two standard buffer solutions. All the experiments were carried out at 25±1°C.

Results

The Acid Dissociation Constants of Calmagite. The dissociation of the free acid of Calmagite may be represented as follows:



The predominant species of Calmagite in the solutions of pH 2—6, pH 9—10, and pH>13 are H_2I^-, HI^{2-}, and I^{3-} respectively. The acid dissociation constants (pk_2 and pk_3) were determined by the spectrophotometric method at an ionic strength of 0.1 or 1.0. Since

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1) 1-(2-Hydroxy-5-methylphenylazo)-2-naphthol-4-sulfonic acid

2) F Lindstrom and H. Diehl, *Anal. Chem.*, **32**, 1123 (1960).

3) M. Kodama and K. Miyamoto, This Bulletin, **42**, 835 (1969).

the sulfonic acid group is a strong acid, the pk_1 could not be measured. The values of pk_2 and pk_3 given in Table 2 agree well with those of Lindstrom and Diehl.

The Formation Constants of Zinc(II)-Calmagite Chelates. Calmagite forms a 1 : 1 chelate with zinc when the concentration of zinc is in a sufficient excess compared with that of Calmagite. In the vicinity of pH 6, the predominant species of the free ligand being H_2I^-, the formation of ZnI^- is expressed as follows, and the equilibrium constant is given by Eq. (1) (The charge will be omitted in the equations for the sake of simplicity):

$$Zn^{2+} + H_2I^- \overset{K}{\rightleftharpoons} ZnI^- + 2H^+$$

$$K = \frac{[ZnI][H]^2}{[Zn][H_2I]} \qquad (1)$$

The absorbance of the solutions containing Calmagite and about a hundredfold excess of zinc(II) were measured at 550 nm, where the difference in absorbance between ZnI^- and H_2I^- is sufficiently large. The variation in the absorbance with the pH is shown in Table 1. From these data, the value of the equilibrium constant, K, was evaluated by means of Hildebrand-Reilley's method[4] and the formation constant, K_{ZnI}, was calculated from K and the acid dissociation constants of Calmagite, k_2 and k_3:

TABLE 1. ABSORBANCE OF 1 : 1 ZINC-CALMAGITE CHELATE IN SOLUTIONS OF VARIOUS pH'S[a)]

pH	Absorbance at 550 nm	pH	Absorbance at 550 nm
5.89	0.670	5.22	0.594
5.59	0.652	5.09	0.579
5.46	0.627	4.89	0.555
5.35	0.609		

a) $C_{Zn}=2.00\times10^{-3}$ mol/l, $C_I=2.86\times10^{-5}$ mol/l, Acetate buffer, $\mu=1.0$ (KNO_3), 25°C, Cell length 1 cm.

$$K_{ZnI} = \frac{[ZnI]}{[Zn][I]} = \frac{K}{k_2 \times k_3} \qquad (2)$$

Zinc(II) forms a 1 : 2 chelate with Calmagite at high pH values (pH>9) in the presence of a large excess of the ligand. The absorption spectra of the solutions containing 1.00×10^{-5} mol/l of zinc and 4.00×10^{-5} mol/l of Calmagite in the pH range from 9 to 10.5 (buffered with potassium hydroxide and boric acid) are shown in Fig. 1. Curves 1 and 5 are the absorption spectra of HI^{2-} and ZnI_2^{4-} respectively. From the absorbance at 640 nm, where the difference in absorbance between the ligand and the zinc chelate is large, the total concentration of the ligand combined with the zinc can be evaluated. The absorption spectra presented by Curves 2—4 show the successive formation of ZnI^- and ZnI_2^{4-} chelates. Under these experimental conditions, the concentration of the free zinc ion is negligible and the following stoichiometric relationships hold:

$$C_{Zn} = [ZnI] + [ZnI_2] \qquad (3)$$

$$C_I = [ZnI] + 2[ZnI_2] + [HI] \qquad (4)$$

where C_{Zn} and C_I are the analytical concentrations of zinc and Calmagite respectively and where [HI] is the total concentration of Calmagite not combined with the zinc ion.

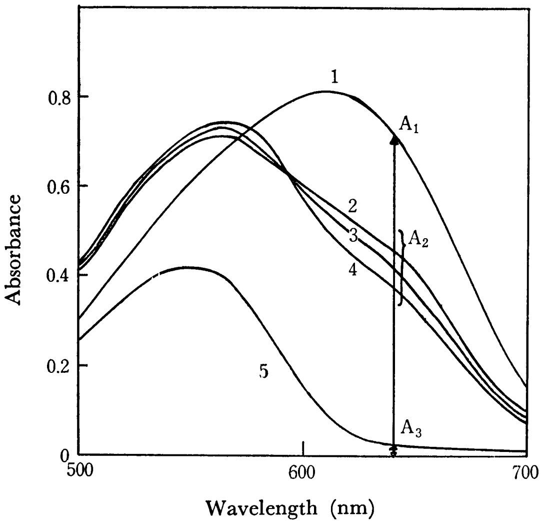

Fig. 1. Absorption spectra of zinc-Calmagite chelates.
$C_I=4.01\times10^{-5}$ mol/l, $C_{Zn}=1.00\times10^{-5}$ mol/l
1: Calmagite only, pH 10.10, 2: pH 9.42, 3: pH 10.02, 4: pH 10.64, 5: ZnI_2 (against reagent blank)

The [HI] values under the given conditions were calculated from the absorbances, A_1, A_2, and A_3, shown in Fig. 1. By representing the molar absorptivity of the ligand, HI^{2-}, and the chelates, ZnI^- and ZnI_2^{4-}, as ε_{HI}, ε_{ZnI}, and ε_{ZnI_2} respectively, we obtain:

$$A_1 = \varepsilon_{HI}C_I \qquad (5)$$

$$A_2 = \varepsilon_{HI}[HI] + \varepsilon_{ZnI}[ZnI] + \varepsilon_{ZnI_2}[ZnI_2] \qquad (6)$$

$$A_3 = \varepsilon_{ZnI_2}C_{Zn} \qquad (7)$$

The absorption spectrum of the ZnI_2^{4-} chelate has same shape as that of the ZnI^- chelate, but the molar absorptivity of ZnI_2^{4-} is twice as much as that of ZnI^-:

$$2\varepsilon_{ZnI} = \varepsilon_{ZnI_2} \qquad (8)$$

By combining Eqs. (4)—(8), and by disignating C_I/C_{Zn} as a, the total concentration of the free ligand is given by Eq. (9):

$$[HI] = \frac{(2A_2 - aA_3)C_I}{2A_1 - aA_3} \qquad (9)$$

By substituting [HI] into Eqs. (3) and (4), we can obtain $[ZnI_2]$ and [ZnI] under the given conditions.

The successive formation constant of ZnI_2^{4-} is defined by Eq. (10):

$$K_{ZnI_2} = \frac{[ZnI_2]}{[ZnI][I]} \qquad (10)$$

[I] can be calculated by means of Eq. (11):

$$[I] = [HI]k_3/[H] \qquad (11)$$

A plot of log $[ZnI_2]/[ZnI]$ *vs.* pI gave a straight line with a slope of −1, log K_{ZnI_2} was evaluated from the x-intercept.

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[4] G. P. Hildebrand and C. N. Reilley, *Anal. Chem.*, **29**, 258 (1957).

Table 2. Acid dissociation constants and complex formation constants of zinc-calmagite at 25°C

Acid dissociation constants		
pk_2	pk_3	Ionic strength
7.92	12.50	0.1 (KNO_3)
7.84	12.08	1.0 (KCl)

Complex formation constants				
log K_{ZnI}	log K_{ZnI_2}	log K^X_{ZnIX}	log $K^X_{ZnIX_2}$	Ionic strength
12.52	7.71			0.1 (KNO_3)
11.75	7.82			1.0 (KNO_3)
11.57		2.09	1.70	1.0 (KNO_3)

The successive formation constants, K_{ZnI} and K_{ZnI_2}, thus obtained are listed in Table 2.

The Formation of Mixed Ligand Complexes. The absorption spectra of 1 : 1 zinc-Calmagite chelates shift to longer wavelengths in an ammoniacal medium. Therefore, it is supposed that zinc may form the mixed ligand complexes, $ZnIX_n^-$, with Calmagite, I^{3-}, and with ammonia, X.

If the mixed ligand complexes are formed, the over-all formation constant of mixed ligand complexes can be defined by Eq. (12):

$$\beta_{ZnIX_n} = \frac{[ZnIX_n]}{[ZnI][X]^n} \tag{12}$$

and the total concentration of the zinc-Calmagite chelates [(ZnI)′] is given by Eq. (13):

$$\begin{aligned}[(ZnI)'] &= [ZnI] + [ZnIX] + [ZnIX_2] + \cdots + [ZnIX_n] \\ &= [ZnI]\alpha_{ZnI(X)} \end{aligned} \tag{13}$$

where:

$$\alpha_{ZnI(X)} = 1 + \sum_{n=1}^{n} \beta_{ZnIX_n}[X]^n \tag{14}$$

Since zinc ion forms ammine complexes in an ammoniacal medium, the total concentration of zinc not combined with Calmagite, [Zn′] is represented by Eq. (15):

$$\begin{aligned}[Zn'] &= [Zn] + [ZnX] + [ZnX_2] + \cdots + [ZnX_m] \\ &= [Zn]\alpha_{Zn(X)} \end{aligned} \tag{15}$$

$$\alpha_{Zn(X)} = 1 + \sum_{m=1}^{m} \beta_m[X]^m \tag{16}$$

where β_m is the over-all formation constant of zinc ammine complexes. Taking into account the protonation of Calmagite,

$$[I'] = [I]\alpha_{I(H)} \tag{17}$$

and:

$$\alpha_{I(H)} = 1 + \frac{[H]}{k_3} + \frac{[H]^2}{k_2k_3} \tag{18}$$

The conditional formation constant of the zinc-Calmagite chelate is given by Eq. (19)

$$K_{Zn'I'(ZnI)'} = \frac{[(ZnI)']}{[Zn'][I']} \tag{19}$$

The experiments were carried out under the conditions where $C_I = 3.6 \times 10^{-5}$ mol/l, $C_{Zn} = 6.5 \times 10^{-5}$ mol/l, $C_X = 0.1$—1.0 mol/l in the pH range from 7 to 9, and $\mu = 1.0$. Some typical absorption spectra are shown in Fig. 2. The absorbances, A_1, A_2, and A_3, in Fig. 2 are expressed as follows:

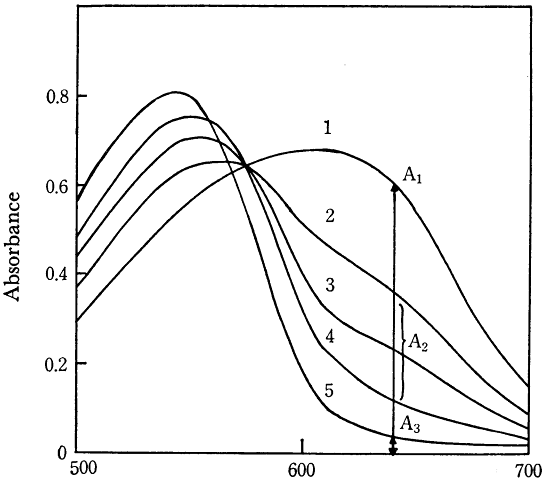

Fig. 2. Absorption spectra of mixed ligand complexes.
$C_I = 3.59 \times 10^{-5}$ mol/l, $C_{Zn} = 6.50 \times 10^{-5}$ mol/l
1: Calmagite only, pH 9.00, 2: pH 8.98, $[NH_3] = 5.02 \times 10^{-1}$ mol/l, 3: pH 9.00, $[NH_3] = 2.96 \times 10^{-1}$ mol/l, 4: pH 8.99, $[NH_3] = 1.46 \times 10^{-1}$ mol/l, 5: pH 9.00, $[NH_3] = 0$

$$A_1 = \varepsilon_I C_I \tag{20}$$

$$A_2 = \varepsilon_I[I'] + \varepsilon_{ZnI}[ZnI] + \sum_{n=1}^{n} \varepsilon_{ZnIX_n}[ZnIX_n] \tag{21}$$

$$A_3 = \varepsilon_{ZnI} C_I \tag{22}$$

where ε_I, ε_{ZnI}, and ε_{ZnIX_n} are the molar absorptivities of the free ligand, ZnI^-, and the mixed ligand complex, $ZnIX_n^-$, respectively. From the absorption spectra of ZnI^- and $ZnIX_n^-$, at 640 nm, ε_{ZnI} is found to be almost equal to ε_{ZnIX_n}. Therefore, [I′] can be calculated from the absorbances at 640 nm in a manner analogous to that used in the previous section:

$$[I'] = \frac{(A_2 - A_3)C_I}{A_1 - A_3} \tag{23}$$

Also, [(ZnI)′] and [Zn′] are given by Eqs. (24) and (25):

$$[(ZnI)'] = C_I - [I'] \tag{24}$$

$$[Zn'] = C_{Zn} - [(ZnI)'] \tag{25}$$

If we obtain the [I′] values from experiments, the conditional formation constant, $K_{Zn'I'(ZnI)'}$, under the given conditions can be calculated by means of Eqs. (19), (24) and (25).

By substituting Eqs. (13), (15), and (17) into Eq. (19), the conditional formation constant of mixed ligand complexes can be rewritten as follows:

$$K_{Zn'I'(ZnI)'} = \frac{K_{ZnI}\alpha_{ZnI(X)}}{\alpha_{Zn(X)}\alpha_{I(H)}} \tag{26}$$

Since [X] can be calculated from the total concentration of ammonia ($C_X = [NH_3] + [NH_4^+]$) and the pH value[5)], $\alpha_{Zn(X)}$ in each experiment can be calculated by means of Eq. (16)[6)] and $\alpha_{I(H)}$ can be obtained from the pHs of the solutions by means of Eq. (18). Using Eq. (26), $K_{ZnI}\alpha_{ZnI(X)}$ can be evaluated from $K_{Zn'I'(ZnI)'}$.

The relation of log $K_{ZnI}\alpha_{ZnI(X)}$ and pX[7] is shown in Fig. 3. log $K_{ZnI}\alpha_{ZnI(X)}$ is a function of pX and the curve approaches a straight line with a slope of 2 in the vicinity of pX=0. From these results, it is clear that zinc forms mixed ligand complexes with Calmagite and ammonia. $K_{ZnI}\alpha_{ZnI(X)}$ can be written as Eq. (27):

$$K_{ZnI}\alpha_{ZnI(X)} = K_{ZnI}(1+K^{X}_{ZnIX}[X] + K^{X}_{ZnXI}K^{X}_{ZnIX_2}[X]^2) \tag{27}$$

where:

$$K^{X}_{ZnIX} = \frac{[ZnIX]}{[ZnI][X]}, \qquad K^{X}_{ZnIX_2} = \frac{[ZnIX_2]}{[ZnIX][X]}$$

From the data plotted in Fig. 3, the successive formation constants of the mixed ligand complexes were calculated by means of a HIPAC 103 computer using the least squares method; the following values were thus obtained: log $K_{ZnI}=11.57$, log $K^{X}_{ZnIX}=2.09$, and log $K^{X}_{ZnIX_2}=1.70$.

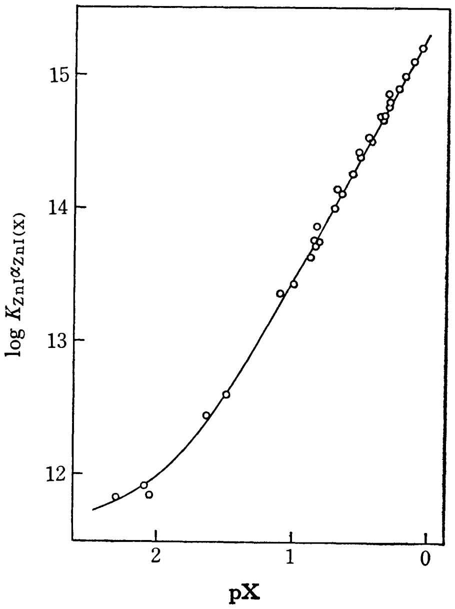

Fig. 3. log $K_{ZnI}\alpha_{ZnI(X)}$ *vs.* pX.

Use as a Metal Indicator for Zinc. In the chelatometric titration of metals, a sharp color change of the indicator is obtained at the equivalence point when the following relationships hold:[8]

$$pM_{\phi=0.5} - pM_{a=0} \gtrsim 3$$

$$pM_{a=2} - pM_{\phi=0.5} \gtrsim 3$$

where $pM_{a=0}$, $pM_{a=2}$, and $pM_{\phi=0.5}$ are pM's before titration, when titrated in a 100% excess and at a 50% color transition respectively.

$pM_{a=0}$, $pM_{a=2}$, and $pM_{\phi=0.5}$ were calculated under various conditions and plotted against the pH (Fig. 4). The optimum conditions for the titration of zinc with EDTA using Calmagite as an indicator can be predicted from the plots of pM *vs.* pH. Zinc forms hydroxide in the range of pH>8.5 when the total concentration of ammonia ($[NH_3]+[NH_4^+]$) is less than 0.1 mol/l. If the total concentration of ammonia is between 0.1 and 0.5 mol/l, it is expected that a sharp color transition of Calmagite can be observed at the equivalence point in the pH range from 8.5 to 10.5. When the concentration of ammonia is 1 mol/l or more, the indicator is considerably discolored before the equivalence point and the color transition after the equivalence point is sluggish.

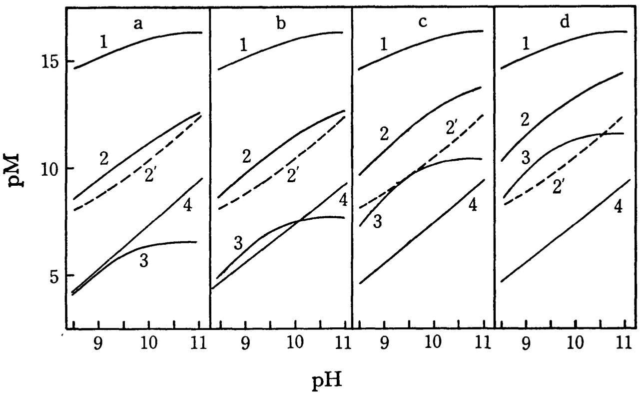

Fig. 4. Optimum conditions for titration of zinc.
$[NH_3]+[NH_4^+]$ (mol/l), a: 0.05, b: 0.1, c: 0.5, d: 1.0
1: $pM_{a=2}$, 2: $pM_{\phi=0.5}$, 3: $pM_{a=0}$, 4: $pM_{Zn(OH)_2}$, 2': $pM_{\phi=0.5}$ if mixed complexes do no form.

These considerations were verified by photometric titration. In Fig. 5 the photometric titration curves are shown. The results of photometric titration are in close agreement with the theoretical results.

Discussion

In a previous paper[9] we reported that indium(III) forms mixed ligand complexes with 2-(2-pyridylazo)-4-methylphenol (PAC) and the acetate ion. It is of much interest now to have found that zinc(II) forms mixed ligand complexes with Calmagite and ammonia.

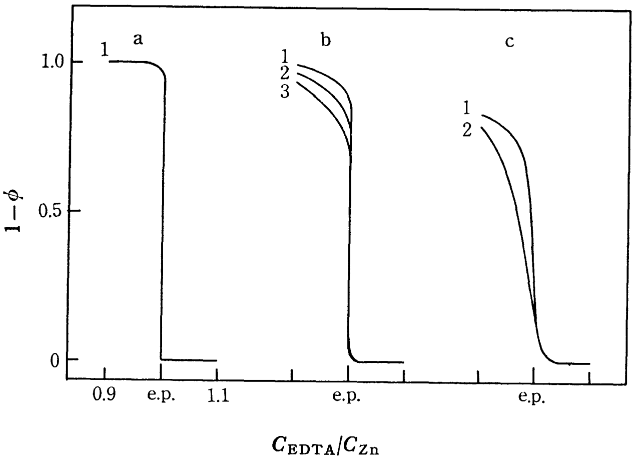

Fig. 5. Photometric titration curves.
$[NH_3]+[NH_4^+]$ (mol/), a: 0.1, b: 0.5, c: 1.0
pH, a: 1; 8.3—10.2, b: 1; 10.5, 2; 9.6, 3; 8.6, c: 1; 10.6, 2; 9.6

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5) $k_{NH_4}=10^{-9.25}$ was used.

6) $\beta_1=10^{2.59}$, $\beta_2=10^{4.91}$, $\beta_3=10^{6.92}$, and $\beta_4=10^{8.62}$ were used.

7) $pX=-\log[X]$

8) M. Tanaka and G. Nakagawa, *Anal. Chim. Acta*, **32**, 123 (1965).

9) H. Wada and G. Nakagawa, *Nippon Kagaku Zasshi*, **89**, 499 (1968).

When the concetration of ammonia is less than 1 mol/l, it has been shown experimentally that less than two moles of ammonia coordinate with the zinc-Calmagite chelate. Since zinc may form octahedral complexes, three moles of ammonia might combine with the zinc-Calmagite chelate at an ammonia concentration of more than 1 mol/l. The successive formation constants of the mixed ligand complexes are smaller than those of corresponding zinc ammine complexes (log $K_{\mathrm{Znx}}=2.59$, log $K_{\mathrm{ZnX_2}}=2.32$).

It has been recognized that the formation of mixed ligand complexes plays an important role in the complexometric titration of zinc. If zinc did not form mixed ligand Complexes with calmagite, the total concentration of ammonia should be kept near 0.1 mol/l. However, the titration can be carried out even in a solution containing a total of 0.5 mol/l of ammonia. The formation of the mixed ligand complexes makes the ammonia concentration in the solutions not critical. In the case of Eriochrome Black T, zinc also forms mixed ligand complexes with ammonia.

Calmagite has some advantageous properties as a metal indicator for the titration of zinc; *i. e.*, the aqueous solution of Calmagite is more stable and the color transition is clearer and sharper than in the case of Eriochrome Black T.