The Theory of the Indicator Transition in Chelatometry

By Genkichi NAKAGAWA and Motoharu TANAKA

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Though various theories have been proposed for the indicator transition in chelatometry, the discussion seems to have been restricted more or less to particular cases; we find hardly any general treatments applicable to every case of chelatometry.[1-5]

In our preceding paper[1] a formula has been proposed for the indicator transition in the chelatometry of a metal using the NY-HA system as an indicator. In the present investigation the effect of a second metal is considered theoretically, and general equations are proposed for the indicator transition in the chelatometry of a metal in the presence of a second metal using HA or the NY-HA system as an indicator.

Theoretical Consideration

The Derivation of the Expressions of the Indicator Transiton.—*Chelatometry Using HA as an Indicator.*—In order to secure a distinct indicator transition in the vicinity of the equivalence point of the chelatometry of M_I, it is necessary for reaction 1.1 to proceed in favor of the right side and, at the same time, for reaction 1.2 to proceed in favor of the left side.

$$M_I{}' + A' \leftrightarrows M_IA \qquad (1.1)^{6)}$$

$$M_IY + A' \leftrightarrows M_IA + Y' \qquad (1.2)$$

From the constant of the (1.1) equilibrium, i.e., the conditional stability constant of M_IA,

$$[M_I]' = \frac{[M_IA]}{[A]'K_{M_I A'}} \qquad (1.3)$$

The constant of the (1.2) equilibrium, which is equal to $K_{M_IA'}/K_{M_IY'}$, is given by the following:

$$\frac{K_{M_IA'}}{K_{M_IY'}} = \frac{[M_IA]\,[Y]'}{[M_IY]\,[A]'}$$

Hence,

$$[Y]' = \frac{[A]'}{[M_IA]}\,\frac{[M_IY]\,K_{M_IA'}}{K_{M_IY'}} \qquad (1.4)$$

Stoicheometric relationships 1.5 through 1.8 hold throughout the titration:

$$C_{M_I} = [M_IY] + [M_IA] + [M_I]' \qquad (1.5)$$

$$C_Y = [M_IY] + [M_{II}Y] + [Y]' \qquad (1.6)$$

$$C_{M_{II}} = [M_{II}Y] + [M_{II}]' \qquad (1.7)$$

$$C_A = [M_IA] + [A]' \qquad (1.8)$$

The side reaction coefficient of the protonation and the formation of $M_{II}Y$, $\alpha_{H,M_{II}(Y)}$, is given by 1.9:

$$\alpha_{H,M_{II}(Y)} = \frac{[M_{II}Y] + [Y]'}{[Y]} \qquad (1.9)^{7)}$$

When Eq. 1.9 is substituted into Eq. 1.6,

$$C_Y = [M_IY] + [Y]\ \alpha_{H,M_{II}(Y)} \qquad (1.10)$$

When Eqs. 1.4 and 1.10 are combined,

$$C_Y = [M_IY]\left(1 + \frac{[A]'}{[M_IA]}\,\frac{K_{M_IA'}\alpha_{H,M_{II}(Y)}}{K_{M_IY}}\right) \qquad (1.11)$$

By substituting Eqs. 1.3 and 1.5 into 1.11, we have

$$C_Y = \left(C_{M_I} - [M_IA] - \frac{[M_IA]}{[A]'}\,\frac{\beta_{(M_I)}\alpha_{H(A)}}{K_{M_IA}}\right) \times\left(1 + \frac{[A]'}{[M_IA]}\,\frac{K_{M_IA}\alpha_{H,M_{II}(Y)}}{K_{M_IY}\alpha_{H(A)}}\right) \qquad (1.12)$$

The indicator transition, ϕ, is defined as:

$$\phi = \frac{[A]'}{C_A} \qquad (1.13)$$

Designating $C_Y/C_{M_I} = a$, we obtain Eq. 1.14 from 1.8, 1.12 and 1.13:

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{\beta_{(M_I)}\alpha_{H(A)}}{C_{M_I}K_{M_IA}} + \frac{\phi}{1-\phi}\,\frac{K_{M_IA}\alpha_{H,M_{II}(Y)}}{K_{M_IY}\alpha_{H(A)}} - \frac{C_A}{C_{M_I}}\left(1-\phi + \phi\frac{K_{M_IA}\alpha_{H,M_{II}(Y)}}{K_{M_IY}\alpha_{H(A)}}\right) - \frac{\beta_{(M_I)}\alpha_{H,M_{II}(Y)}}{C_{M_I}K_{M_IY}} \qquad (1.14)$$

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1) G. Nakagawa and M. Tanaka, *Talanta*, **9**, 917 (1962).

2) J. M. H. Fortuin, P. Karsten and H. L. Kies, *Anal. Chim. Acta*, **10**, 356 (1954).

3) H. Flaschka and S. Khalafalla, *Z. anal. Chem.*, **156**, 401 (1957).

4) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **31**, 887 (1959).

5) H. Flaschka, *Talanta*, **1**, 60 (1958).

6) A is assumed to form a 1:1 chelate with M_I.

7) From the formation constant of $M_{II}Y$, we have

$$\alpha_{H,M_{II}(Y)} = K_{M_{II}Y}[M_I{}^I] + \alpha_{H(Y)}$$

For a more detailed discussion of the concept of the ligand buffer, as well as for the calculation of $\alpha_{H,M_{II}(Y)}$, cf. M. Tanaka, *Anal. Chim. Acta*, **29**, 193 (1963).

Equation 1.14 is a quantitative expression of the indicator transition in the chelatometry of M_I in the presence of M_{II}, using HA as an indictor. Under conditions favorable for the titration, the last term of Eq. 1.14 may be neglected, and, when $C_A \ll C_{M_I}$, the fourth term on the right side of Eq. 1.14 may also be neglected. Therefore,

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{\beta_{(M_I)}\alpha_{H(A)}}{C_{M_I}K_{M_IA}} + \frac{\phi}{1-\phi}\,\frac{K_{M_IA}\alpha_{H,M_{II}(Y)}}{K_{M_IY}\alpha_{H(A)}} \tag{1.15}$$

Near the equivalence point $[M_{II}Y]$ is negligibly small compared with $[M_{II}]'$ in Eq. 1.7, so

$$\alpha_{H,M_{II}(Y)} = K_{M_{II}Y}C_{M_{II}}/\beta_{(M_{II})} + \alpha_{H(Y)}$$

When the formation of $M_{II}Y$ is not appreciable, $\alpha_{H,M_{II}(Y)} = \alpha_{H(Y)}$. The substitution of this relationship into Eq. 1.15 gives an equation for the indicator transition in the absence of a second metal, M_{II}.[4,5]

Chelatometry Using the NY-HA System as an Indicator.—The indicator transition of a chelatometry using the NY-HA system as an indicator should be discussed for the following two cases separately:

a) $K_{M_I'Y'} > K_{N'Y'}$, e.g., the titration of calcium with EDTA, using the Mg-EDTA-Erio T system as an indicator, and b) $K_{N'Y'} > K_{M_I'Y'}$, e. g., the titration of aluminum with EDTA using the Cu-EDTA-PAN system as an indicator.

a) $K_{M_I'Y'} > K_{N'Y'}$. — This case corresponds to the so-called partial replacement titration, in which we consider the following two equilibria:

$$N' + A' \rightleftharpoons NA \tag{2.1}$$

$$NY + A' \rightleftharpoons NA + Y' \tag{2.2}$$

From the constants of equilibria 2.1 and 2.2, we have

$$[N]' = \frac{[NA]}{[A]'K_{N'A'}} \tag{2.3}$$

$$[Y]' = \frac{[A]'}{[NA]}\,\frac{[NY]K_{NA'}}{K_{NY'}} \tag{2.4}$$

Stoicheometric relationships 2.5 through 2.8 hold throughout the titration:

$$C_{M_I} = [M_IY] + [M_I]' \tag{2.5}$$

$$C_Y = [M_IY] + [NY] + [M_{II}Y] + [Y]' \tag{2.6}$$

$$C_N = [NY] + [NA]' + [N]' \tag{2.7}$$

$$C_A = [NA] + [A]' \tag{2.8}$$

N being added as NY, the total concentration of the complexan used as the titrant, C_Y', is given by $C_Y' = C_Y - C_N$. Therefore, from Eqs. 2.5, 2.6 and 2.7, we obtain

$$C_Y' = C_{M_I} - [M_I]' - [N]' + [Y]\alpha_{H,M_{II}(Y)} - [NA] \tag{2.9}$$

From the formation constants of M_IY and NY,

$$\frac{[M_IY]}{[M_I]'K_{M_I'Y}} = \frac{[NY]}{[N]'K_{N'Y}}$$

Therefore,

$$[M_I]' = \frac{C_{M_I}[N]'K_{N'Y}}{K_{M_I'Y}(C_N - [N]') + [N]'K_{N'Y}} \tag{2.10}$$

Substituting Eq. 2.10 into 2.9, we have

$$a = C_Y'/C_{M_I} = 1 - \frac{[N]'}{C_{M_I}} \times \left(1 + \frac{C_{M_I}K_{N'Y}}{K_{M_I'Y}(C_N - [N]') + [N]'K_{N'Y}}\right) + \frac{[Y]\alpha_{H,M_{II}(Y)}}{C_{M_I}} - \frac{[NA]}{C_{M_I}} \tag{2.11}$$

When $K_{M_I'Y'} > K_{N'Y'}$ and $a > 1 - C_N/C_{M_I}$, we can neglect the second term in the parentheses of the second term on the right side of Eq. 2.11. Therefore, by combining Eqs. 2.3, 2.4 and 2.11, we obtain

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{\beta_{(N)}\alpha_{H(A)}}{K_{NA}C_{M_I}} + \frac{\phi}{1-\phi}\,\frac{K_{NA}\alpha_{H,M_{II}(Y)}C_N}{K_{NY}\alpha_{H(A)}C_{M_I}} - \frac{C_A}{C_{M_I}}\left(1-\phi + \phi\frac{K_{NA}\alpha_{H,M_{II}(Y)}}{K_{NY}\alpha_{H(A)}}\right) - \frac{\beta_{(N)}\alpha_{H,M_{II}(Y)}}{K_{NY}C_{M_I}} \tag{2.12}$$

In a favorable condition for the titration, we can neglect the last term on the right side of Eq. 2.12, and, C_{M_I} being generally much greater than C_A, we can also neglect the fourth term. Therefore, we have

$$a = 1 - \frac{1-\phi}{\phi}\,\frac{\beta_{(N)}\alpha_{H(A)}}{K_{NA}C_{M_I}} + \frac{\phi}{1-\phi}\,\frac{K_{NA}\alpha_{H,M_{II}(Y)}C_N}{K_{NY}\alpha_{H(A)}C_{M_I}} \tag{2.13}$$

In the vicinity of the equivalence point, $\alpha_{H,M_{II}(Y)} = K_{M_{II}Y}C_{M_{II}}/\beta_{(M_{II})} + \alpha_{H(Y)}$ in Eq. 2.13, and when the formation of $M_{II}Y$ is not appreciable, $\alpha_{H,M_{II}(Y)} = \alpha_{H(Y)}$.

It should be remembered that Eq. 2.13 holds for $a > 1 - C_N/C_{M_I}$. For $a < 1 - C_N/C_{M_I}$, however, Eq. 2.13 does not hold; we can not neglect the second term in parentheses on the right side of Eq. 2.11. In this case, most Y being combined with M_I, $[N]' \simeq C_N$. Therefore, from Eq. 2.3,

$$1 - \phi = \frac{C_NK_{N'A'}}{C_NK_{N'A'} + 1}$$

The maximum coloration of the indicator is determined by this equation. It then follows that, in order to secure a full coloration of NA before the equivalence point, the $C_{N}K_{N'A'}$ value should be much greater than unity.

b) $K_{N'Y'}>K_{M_{I}'Y'}$.—We shall consider the following two equilibria, the constants of which are denoted as K_1 and K_2:

$$\mathrm{NY} + \mathrm{M_I}' + \mathrm{A}' \overset{K_1}{\rightleftharpoons} \mathrm{M_IY} + \mathrm{NA}$$

$$K_1=\frac{[\mathrm{M_IY}]\,[\mathrm{NA}]}{[\mathrm{NY}]\,[\mathrm{M_I}]'\,[\mathrm{A}]}=\frac{K_{\mathrm{M_I'Y}}K_{\mathrm{NA'}}}{K_{\mathrm{NY}}} \tag{2.14}$$

$$\mathrm{NY} + \mathrm{A}' \overset{K_2}{\rightleftharpoons} \mathrm{NA} + \mathrm{Y}'$$

$$K_2=\frac{[\mathrm{NA}]\,[\mathrm{Y}]'}{[\mathrm{NY}]\,[\mathrm{A}]'}=\frac{K_{\mathrm{NA}}'}{K_{\mathrm{NY}}'} \tag{2.15}$$

From expressions 2.14 and 2.15, we have

$$[\mathrm{M_I}]'=\frac{[\mathrm{M_IY}]\,[\mathrm{NA}]}{[\mathrm{NY}]\,[\mathrm{A}]'K_1} \tag{2.16}$$

$$[\mathrm{Y}]'=\frac{[\mathrm{A}]'\,[\mathrm{NY}]K_2}{[\mathrm{NA}]} \tag{2.17}$$

The following stoicheometric relationships, 2.18 through 2.22, hold throughout the titration:

$$C_{\mathrm{M_I}} = [\mathrm{M_IY}] + [\mathrm{M_I}]' \tag{2.18}$$

$$C_{\mathrm{Y}} = [\mathrm{M_IY}] + [\mathrm{M_{II}Y}] + [\mathrm{NY}] + [\mathrm{Y}]' \tag{2.19}$$

$$C_{\mathrm{M_{II}}} = [\mathrm{M_{II}Y}] + [\mathrm{M_{II}}]' \tag{2.20}$$

$$C_{\mathrm{N}} = [\mathrm{NY}] + [\mathrm{NA}] + [\mathrm{N}]' \tag{2.21}$$

$$C_{\mathrm{A}} = [\mathrm{NA}] + [\mathrm{A}]' \tag{2.22}$$

N being generally added as NY, the total concentration of the complexan used as the titrant, C_{Y}', is given by the following:

$$C_{\mathrm{Y}}' = C_{\mathrm{Y}} - C_{\mathrm{N}} \tag{2.23}$$

When N does not form any appreciable complexes other than NY and NA, [N]′ can be neglected in Eq. 2.21. Therefore, by combining Eqs. 1.9, 2.19 and 2.23, we have

$$C_{\mathrm{Y}}' = [\mathrm{M_IY}] + [\mathrm{Y}]\,\alpha_{\mathrm{H,M_{II}(Y)}} - [\mathrm{NA}] \tag{2.24}$$

Substituting Eq. 2.17 into 2.24,

$$C_{\mathrm{Y}}'=[\mathrm{M_IY}]+\frac{[\mathrm{A}]'}{[\mathrm{NA}]}\,\frac{[\mathrm{NY}]\,K_2\alpha_{\mathrm{H,M_{II}(Y)}}}{\alpha_{\mathrm{H(Y)}}} - [\mathrm{NA}] \tag{2.25}$$

On the other hand, from Eqs. 2.16 and 2.18,

$$C_{\mathrm{M_I}} = [\mathrm{M_IY}]\left(1+\frac{[\mathrm{NA}]}{[\mathrm{A}]'}\,\frac{1}{[\mathrm{NY}]\,K_1}\right) \tag{2.26}$$

By combining Eqs. 2.25 and 2.26, we have

$$C_{\mathrm{Y}'} = C_{\mathrm{M_I}}\Big/\left(1+\frac{[\mathrm{NA}]}{[\mathrm{A}]'}\,\frac{1}{[\mathrm{NY}]\,K_1}\right) + \frac{[\mathrm{A}]'}{[\mathrm{NA}]}\,\frac{[\mathrm{NY}]\,K_2\alpha_{\mathrm{H,M_{II}(Y)}}}{\alpha_{\mathrm{H(Y)}}} - [\mathrm{NA}] \tag{2.27}$$

Under conditions favorable for titration, $[\mathrm{NA}]/[\mathrm{A}]'[\mathrm{NY}]K_1$ is much smaller than unity in the vicinity of the equivalence point. Since $C_{\mathrm{M_I}}$ is generally much greater than C_{A}, the fourth term on the right side of Eq. 2.27 can be neglected. Moreover, when C_{N} is much greater than C_{A}, [NY] may be regarded as C_{N}. Therefore,

$$a=1-\frac{1-\phi}{\phi}\,\frac{K_{\mathrm{NY}}\beta_{(\mathrm{M_I})}\alpha_{\mathrm{H(A)}}}{K_{\mathrm{M_IY}}K_{\mathrm{NA}}C_{\mathrm{N}}} + \frac{\phi}{1-\phi}\,\frac{K_{\mathrm{NA}}\alpha_{\mathrm{H,M_{II}(Y)}}C_{\mathrm{N}}}{K_{\mathrm{NY}}\alpha_{\mathrm{H(A)}}C_{\mathrm{M_I}}} \tag{2.28}$$

In the vicinity of the equivalence point, $\alpha_{\mathrm{H,M_{II}(Y)}}$ is given by the following:

$$\alpha_{\mathrm{H,M_{II}(Y)}}=K_{\mathrm{M_{II}Y}}C_{\mathrm{M_{II}}}/\beta_{(\mathrm{M_{II}})} + \alpha_{\mathrm{H(Y)}}$$

and, when the formation of $\mathrm{M_{II}Y}$ is not appreciable, $\alpha_{\mathrm{H,M_{II}(Y)}}=\alpha_{\mathrm{H(Y)}}$.

A General Discussion of the Indicator Transition in the Vicinity of the Equivalence Point of Chelatometry.—In Eqs.1.15, 2.13 and 2.28, ϕ is a value expressing the indicator transition, and the second term is mainly concerned with the color transition before the equivalence point, while the third is mainly concerned with the color transition after the equivalence point.

Equations 1.15, 2.13 and 2.28 can be rewritten as the following general form:

$$a=1-\frac{1-\phi}{\phi}f_1+\frac{\phi}{1-\phi}f_2$$

Thus the indicator transition near the equivalence point in any chelatometry is determined by a combination of f_1 and f_2 values; the lower the values of f_1 and f_2, the sharper the indicator transition.

Now it should be noted that the value of $f_1 f_2$ is independent of the indicator characteristics and is given by the following:

$$f_1 f_2=\frac{\alpha_{\mathrm{H,M_{II}(Y)}}\beta_{(\mathrm{M_I})}}{K_{\mathrm{M_IY}}C_{\mathrm{M_I}}}$$

Thus, if $K_{\mathrm{M_{II}'Y'}}$ is sufficiently low, a distinct indicator transition will be obtained even for a high value of $C_{\mathrm{M_{II}}}/C_{\mathrm{M_I}}$. From Eqs. 1.15, 2.13 and 2.28, it can easily be seen that $\mathrm{M_{II}}$ hardly affects the indicator transition *before* the equivalence point. However, the higher the value of $\alpha_{\mathrm{H,M_{II}(Y)}}$ or $K_{\mathrm{M_{II}'Y'}}C_{\mathrm{M_{II}}}$, the less distinct the indicator transition *after* the equivalence point. ϕ or $1-\phi$ versus a diagrams drawn for various combinations of f_1 and f_2 values facilitate the establishment of the optimum conditions for a given problem; the computation of f_1 and f_2 values for a given

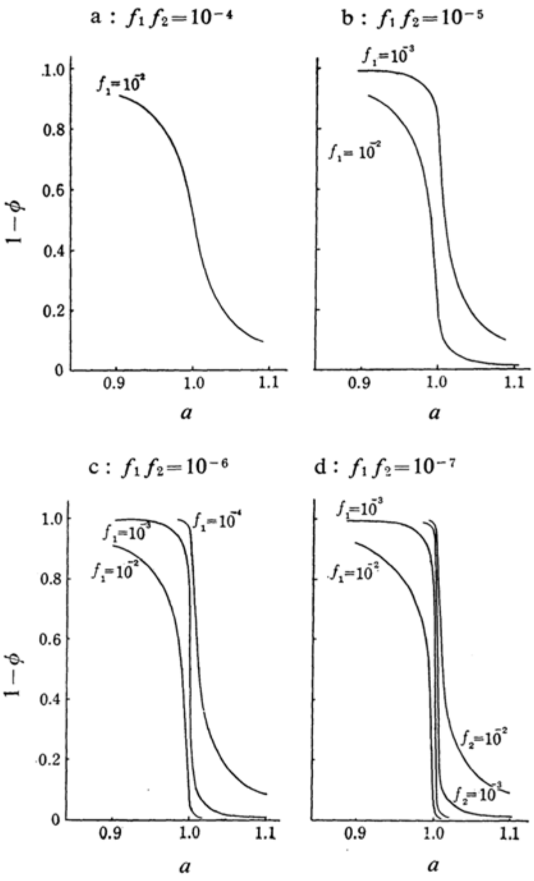
a : $f_1 f_2=10^{-4}$ b : $f_1 f_2=10^{-5}$ c : $f_1 f_2=10^{-6}$ d : $f_1 f_2=10^{-7}$

Fig. 1. Theoretical indicator transition for various couples of f_1 and f_2.

system makes possible the prediction of the indicator transition (Fig. 1).

We would like to emphasize that Eqs. 1.15, 2.13 and 2.28 make possible a theoretical consideration of the indicator transition in any type of chelatometry using HA or the NY-HA system as an indicator.

Applicability of the Theory

The above theory has been confirmed experimentally in some familiar examples of the titration of alkaline earths with EDTA, using Erio T as an indicator.

HA as an Indicator.—The titration of magnesium with EDTA, using Erio T as an indicator.

a) In the absence of a second metal.

Condition: $C_{M_I}=C_{Mg}=10^{-3}$M; $C_{M_{II}}=0$; pH $=10$.[8] Using $\log K_{MgY}=8.69$ and $\log K_{MgA'}$ (pH$=10$)$=5.44$,[9] f_1 and f_2 are computed thus:

$$f_1=\frac{1}{K_{MgA'}C_{Mg}}=10^{-2.44}\,;\quad f_2=\frac{K_{MgA'}}{K_{MgY'}}=10^{-2.80}$$

From these values, a distinct indicator transition is anticipated in the vicinity of the equivalence point (cf. Fig. 1).

b) In the presence of sodium.

When $C_{M_{II}}=C_{Na}=1$ M, f_1 is the same as in a) and, from $\log K_{NaY}=1.66$,

$$f_2=\frac{K_{MgA'}}{K_{MgY'}}(K_{NaY'}C_{Na}+1)=10^{-1.56}$$

Thus the discoloration of Mg-Erio T after the equivalence point will become somewhat sluggish. However, the visual titration of magnesium in the presence of 1 M sodium is possible.[10]

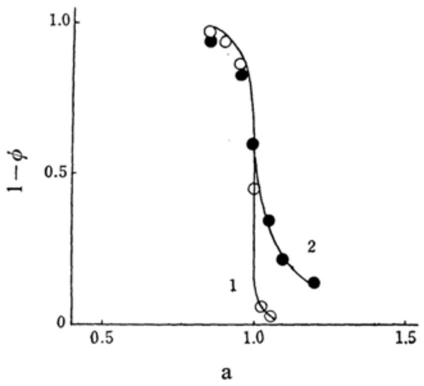

Fig. 2. Indicator transition of the titration of magnesium using Erio T as an indicator.
—— Theoretical indicator transition:
Curve 1: Na=0, Curve 2: Na=1 M
○● Experimental values:
○: Na=0, ●: Na=1 M

Figure 2 shows the results of the photometric titration of magnesium, using Erio T as an indicator, as well as the theoretical indicator transition curve. The experimental results agree well with the theoretical curves after the equivalence point. The discordance between the observed and the theoretical curves before the equivalence point may be attributable to the decomposition of Erio T, which is accelerated in the presence of sodium.[11]

The purity of commercial preparations of Erio T is often very low, and the decomposition of impure Erio T is particularly fast. A method for the purification of Erio T has

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[8] At a pH value of 10 neither hydrolysis nor the ammine formation of magnesium needs to be taken into consideration.

[9] G. Schwarzenbach, "Die komplexometrische Titration," Ferdinand Enke Verlag, Stuttgart (1955), p. 27.

[10] Using an indicator such as Erio T, of which the contrast of metallized and unmetallized indicator is sufficiently large, visual titration is possible with values of f_1 and f_2 up to about $10^{-1.5}$.

[11] G. Nakagawa and M. Tanaka, unpublished results.

been described[12]; in the present investigation, however, we employed Erio T purified by the following simplified procedure: 20 g. of commercial Erio T (Dojindo Chemical Co., Kumamoto) are washed five times with 50 ml. of 2 N hydrochloric acid. The desalted dye is then air-dried and recrystallized from dimethylformamide. Though the obtained dimethylammonium salt of Erio T is not very pure, it is satisfactory for all practical purposes.

The NY-HA System as an Indicator.—*i) Partial Replacement Titration,* $K_{M_I'Y'} > K_{N'Y'}$.—The titration of calcium, with EDTA using the MgY-ErioT system as an indicator.

a) In the absence of a second metal.

Condition: $C_{M_I} = C_{Ca} = 10^{-3}$M; $C_{M_{II}} = 0$; pH $= 10$. Using the values log $K_{CaY} = 10.70$, K_{MgY} and $K_{MgA'}$ (pH$=10$), f_1 and f_2 in Eq. 2.13 are computed:

$$f_1 = \frac{1}{K_{MgA'} C_{Ca}} = 10^{-2.44}$$

$$f_2 = \frac{K_{MgA'} C_{Mg}}{K_{MgY} C_{Ca}} = 10^{0.20} C_{Mg}$$

f_1, f_2 and $(1-\phi)_{\max}$ values for various values of C_{Mg} are given in Table I.

TABLE I. f_1 AND f_2 FOR VARIOUS VALUES OF C_{Mg} IN THE CHELATOMETRY OF CALCIUM USING MgY-Erio T SYSTEM AS AN INDICATOR

C_{Mg}, M	log f_1	log f_2	$(1-\phi)_{\max}$
10^{-3}	-2.44	-2.80	0.996
10^{-4}	-2.44	-3.80	0.965
10^{-5}	-2.44	-4.80	0.734

From Table I it may easily be deduced that about 10^{-4}M of magnesium will give the best results.

b) In the presence of sodium.

The indicator transition is considered for the chelatometry of calcium in the presence of 1M sodium using C_{Mg} of 10^{-4}M, which gives the best indicator transition in the absence of a second metal. f_1 and $(1-\phi)_{\max}$ are the same as in i a), and

$$f_2 = \frac{K_{MgA'} C_{Mg}}{K_{MgY'} C_{Ca}} (K_{NaY'} C_{Na} + 1) = 10^{-2.57}$$

It is evident that calcium is successfully titrated in the presence of 1M sodium.

ii) $K_{N'Y'} > K_{M_IY'}$.—The titration of barium with EDTA, using the MgY-Erio T system as an indicator.

a) In the absence of a second metal.

Condition: $C_{M_I} = C_{Ba} = 10^{-3}$M; $C_{M_{II}} = 0$; pH $= 10$. Calculation gives the following values:

$$f_1 = 10^{-4.51}/C_{Mg} \text{ and } f_2 = 10^{0.20} C_{Mg}$$

f_1 and f_2 for various values of C_{Mg} are given in Table II. Table II also shows that 5×10^{-3}M of magnesium will give the best indicator

TABLE II. f_1 AND f_2 FOR VARIOUS VALUES OF C_{Mg} IN THE CHELATOMETRY OF BARIUM USING MgY-Erio T SYSTEM AS AN INDICATOR

C_{Mg}, M	log f_1	log f_2
10^{-2}	-2.51	-1.80
5×10^{-3}	-2.21	-2.10
2×10^{-3}	-1.81	-2.50
10^{-3}	-1.51	-2.80
10^{-5}	-0.51	-3.80

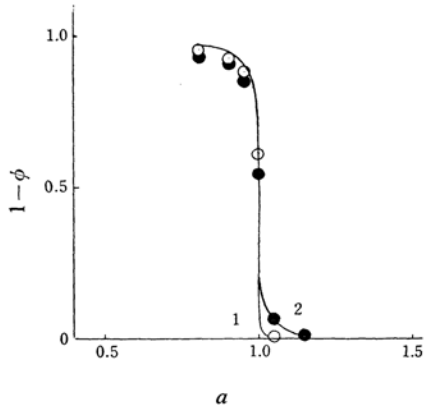

Fig. 3. Indicator transition of the titration of calcium using MgY-Erio T system as an indicator.

—— Theoretical indicator transition:
Curve 1: Na=0, Curve 2: Na=1 M
○● Experimental values:
○: Na=0, ●: Na=1 M

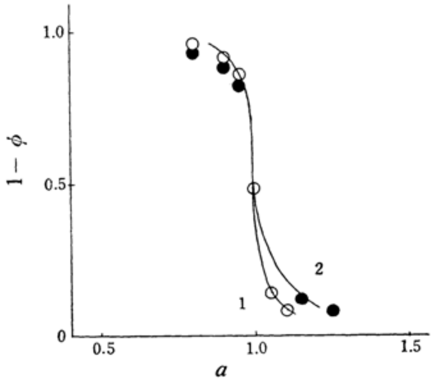

Fig. 4. Indicator transition of the titration of barium using MgY-Erio T system as an indicator.

—— Theoretical indicator transition:
Curve 1: Na=0, Curve 2: Na=1 M
○● Experimental values:
○: Na=0, ●; Na=1 M

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[12] H. Diehl and F. Lindstrom, *Anal. Chem.*, **31**, 414 (1959).

transition; this is not, however, very satisfactory.

The discussion given under i), agrees well with that of Schwarzenbach.[13]

b) In the presence of sodium.

A similar consideration has been made for $C_{Mg}=5\times10^{-3}$M, $C_{Na}=0.1$ N. The computed values of f_1 and f_2 are as follows:

$$f_1=10^{-2.21} \text{ and } f_2=10^{-1.68}$$

Judging from these values, it is anticipated that the presence of 0.1M sodium may be tolerable in the visual titration of barium, using MgY-Erio T as an indicator. However, a larger amount of sodium will make the indicator transition sluggish.

Figures 3 and 4 show the results obtained for calcium and barium. The experimental results agree well with the theoretical indicator transition after the equivalence point. As has been indicated, the discordance between the observed and the theoretical curves before the equivalence point may be attributable to the decomposition of Erio T.[14]

It is true that the difference in ionic strength or the addition of an organic solvent may modify the constants involved, but in the ordinary range of the usual experimental conditions the modification of the constants rarely exceeds one logarithm unit. Therefore, for most cases, the titration can be predicted on a sound theoretical basis by the proposed equations.

Summary

General equations have been proposed for the indicator transition in the chelatometry of a metal in the presence of other metals, using HA or the NY-HA system as an indicator. The validity of these equations has been confirmed experimentally in several examples of practical importance. If the constants involved are all available, it is possible, by the aid of the proposed equations, to predict the optimum conditions for any type of chelatometry.

List of Symbols

Symbols used are summarized below in the order of appearance in the text. Most of them are of current use in the literature, but in order to avoid confusions they are defined once when appeared for the first time.

M, N	Metal
Y	Complexan
NY	Chelate of metal N with complexan Y
HA	Metallochromic indicator
M'	Metal M not combined with Y and A
Y'	Y not combined with M_I
$[M]'$, etc.	Concentration of M', etc.
K_{MY}, etc.	Stability constant of MY, etc.
$\alpha_{H(Y)}$	Side reaction coefficient of protonation of Y.
$\alpha_{H(A)}$	Side reaction coefficient of protonation of A: $\alpha_{H(A)}=[A]'/[A]$
$\alpha_{H,M_{II}(Y)}$	Side reaction coefficient of protonation and chelation with M_{II} of Y
$\beta_{(M)}$	Side reaction coefficient of complex formation of M with auxiliary complexing agents: $\beta_{(M)}=[M]'/[M]$
$K_{M'Y'}$ etc.	Conditional stability constant of MY: $K_{M'Y'}=K_{MY}/\alpha_{H(Y)}\beta_{(M)}$, $K_{M'Y}=K_{MY}/\beta_{(M)}$, $K_{MY'}=K_{MY}/\alpha_{H(Y)}$
C_M, etc.	Total concentration of M, etc.
$C_{Y'}$	Total concentration of Y used as titrant
a	Fraction titrated: C_Y/C_{MI}
ϕ	Indicator transition: $[A]'/C_A$

Laboratory of Analytical Chemistry
Nagoya Institute of Technology
Showa-ku, Nagoya (G. N.)

Laboratory of Analytical Chemistry
Faculty of Science, Nagoya University
Chikusa-ku, Nagoya (M. T.)

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[13] Schwarzenbach, op. cit., p. 53.

[14] The decomposition of impure Erio T is much more considerable.