Photometric Determination of Indicator End Points in Complexometric Titrations

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(Received August 13, 1958)

In photometric titrations with an indicator, the color does not develop linearly with the titrant added. This characteristic has been elucidated by a mathematical treatment of complexometric titration with specific indicator for a certain metal[1].

In a previous communication[2], the present authors proposed a graphical method for determining indicator end point in the complexometric titration by a photometric technique and applied it with success to the titration of magnesium with disodium salt of ethylenediaminetetraacetic acid (Complexon III) using Eriochrome Black T (EBT) as indicator. This method is, however, an approximate one and therefore its utility and limitation will be discussed in the present paper.

Theoretical

List of Principal Symbols.—

m_t, total concentration of metal in titration system

i_t, total concentration of indicator in titration system

c_t, total concentration of titrant in titration system

$\mu=c_t/m_t$, relative concentration of titrant

$\alpha=[I^*]/i_t$, ratio of $[I^*]/([MI]+[I^*])$

$[I^*]=[I]+[HI]+[H_2I]+\cdots\cdots$, sum of the concentrations of metal-free indicator components

$[Y^*]=[Y]+[HY]+[H_2Y]+\cdots\cdots$, sum of the concentrations of metal-free titrant

$K^*_Y=[MY]/[M][Y^*]$, apparent stability constant

$K^*_I=[MI]/[M][I^*]$, apparent indicator constant

A_s, absorbancy during the course of titration

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[1] J. M. H. Fortuin, P. Karsten and H. L. Kies, *Anal. Chim. Acta*, **10**, 365 (1954).

[2] S. Musha, M. Munemori and K. Ogawa, This Bulletin, **30**, 675 (1957).

$A_{s\mathrm{I}}$, absorbancy of metal-free indicator
$A_{s\mathrm{MI}}$, absorbancy of metal-indicator complex
V, volume of titrant solution added, in ml.
V_{eq}, volume of titrant solution equivalent to the total concentration of metal, in ml.
V_0, volume of metal ion solution to be titrated, in ml.
C, molarity of titrant

General Expression and Approximate Expression. — In titrating the metal ion with such a reagent as Complexon-III in an aqueous system, there are the following equilibria:

$$\mathrm{M}+\mathrm{Y}^*=\mathrm{MY} \quad \text{and} \quad \mathrm{M}+\mathrm{I}^*=\mathrm{MI} \tag{1}$$

From K_{Y}^* and K_{I}^* it follows that:

$$[\mathrm{MY}]=K_{\mathrm{Y}}^*[\mathrm{M}]\,[\mathrm{Y}^*] \tag{2}$$

$$[\mathrm{MI}]=K_{\mathrm{I}}^*[\mathrm{M}]\,[\mathrm{I}^*] \tag{3}$$

On the other hand, m_t, c_t and i_t are expressed by the following equations:

$$m_t=[\mathrm{M}]+[\mathrm{MY}]+[\mathrm{MI}] \tag{4}$$

$$c_t=[\mathrm{MY}]+[\mathrm{Y}^*] \tag{5}$$

$$i_t=[\mathrm{MI}]+[\mathrm{I}^*] \tag{6}$$

From Eqs. 2, 3, 4, 5 and 6, the following relationship is derived.

$$c_t=m_t-[\mathrm{MI}]\left(1+\frac{1}{K_{\mathrm{I}}^*[\mathrm{I}^*]}\right)+[\mathrm{I}^*]\frac{K_{\mathrm{I}}^*}{K_{\mathrm{Y}}^*}\left\{\frac{m_t}{[\mathrm{MI}]}-\left(1+\frac{1}{K_{\mathrm{I}}^*[\mathrm{I}^*]}\right)\right\} \tag{7}$$

By replacing Eq. 7 by the relative values μ and α, comes the following equation:

$$\mu=1-\frac{1}{m_t}(1-\alpha)\left(i_t+\frac{1}{\alpha K_{\mathrm{I}}^*}\right)+\alpha\frac{K_{\mathrm{I}}^*}{K_{\mathrm{Y}}^*}\left\{\frac{1}{1-\alpha}-\frac{1}{m_t}\left(i_t+\frac{1}{\alpha K_{\mathrm{I}}^*}\right)\right\} \tag{8}$$

Eq. 8 is the general expression for the spectrophotometric titration curve and will be called *general equation.*

Now, if $[\mathrm{Y}^*]$ and i_t are so small that they can be neglected in the course of titration, Eqs. 4 and 5 are converted into the followings:

$$m_t=[\mathrm{M}]+[\mathrm{MY}] \tag{9}$$

$$c_t=[\mathrm{MY}] \tag{10}$$

From Eqs. 2, 3, 9 and 10 it follows that:

$$c_t=m_t-\frac{1}{K_{\mathrm{I}}^*}\frac{[\mathrm{MI}]}{[\mathrm{I}^*]} \tag{11}$$

If the dilution of solution by titrant is neglected, Eq. 12 will be obtained by substituting Eq. 11 with V and V_{eq}:

$$V=V_{eq}-\frac{V_0}{C}\frac{1}{K_{\mathrm{I}}^*}\frac{[\mathrm{MI}]}{[\mathrm{I}^*]} \tag{12}$$

Values of $[\mathrm{MI}]/[\mathrm{I}^*]$ can be computed from the absorbancy readings by means of the following equation:

$$[\mathrm{MI}]/[\mathrm{I}^*]=(A_{s\mathrm{I}}-A_s)/(A_s-A_{s\mathrm{MI}}) \tag{13}$$

If $(A_{s\mathrm{I}}-A_s)/(A_s-A_{s\mathrm{MI}})$ is plotted against V will result a straight line whose intercept on the V-axis is equal to V_{eq}[2]. By replacing Eq. 11 by μ and α, comes Eq. 14:

$$\mu=1-\frac{1}{m_t}\frac{1}{K_{\mathrm{I}}^*}\frac{1-\alpha}{\alpha} \tag{14}$$

Eq. 14 is the approximate expression for the spectrophotometric titration curve and will be called *approximate equation.*

Discussion

On the basis of general equation, Fortuin et al.[1] discussed the condition to be fulfilled for the accurate determination of indicator end point in complexometric titration by a photometric method. In the present paper, however, we shall discuss the conditions under which the approximate equation is established within experimental errors.

When Eq. 14 is compared with Eq. 8, i_t and K_{Y}^* are omitted in Eq. 14, and therefore the effects of these variables on the deviation of the approximate equation from the general equation will be mainly examined.

If the magnitudes of m_t, i_t, K_{Y}^* and K_{I}^* are assigned in Eq. 8, α and hence $(1-\alpha)/\alpha$ can be evaluated as a function of μ. The curves in Figs. 2 and 4 illustrate the manner in which α changes with μ for the systems defined by Tables I and II, respectively. Corresponding curves in Figs. 1 and 3 illustrate the variation of $(1-\alpha)/\alpha$ with μ. Line A_0 in Fig. 1 and line B_0 in Fig. 3 show the plots obtained by Eq. 14.

1) Effect of i_t.—The effect of the magnitude of i_t was examined when K_{I}^* is much smaller than K_{Y}^*. From Fig. 1 it is seen that the deviation of the approximate equation from the general equation becomes greater at higher indicator concentration. Therefore, it may be concluded that in order to estimate μ with precision of 1%, the molarity of the indicator must be ten times smaller than $1/K_{\mathrm{I}}^*$ in numero. Fig. 2, which represents actual behavior of photometric titration curve, shows ambiguous end point at higher indicator concentration.

2) Effect of K_{Y}^*. — The effect of the magnitude of K_{Y}^* was examined when the

TABLE I

Curve	$m_t\times10^2$	$i_t\times10^5$	$K_I^*\times10^{-4}$	$K_Y^*\times10^{-12}$
A_1	1/3	3	1/8	4
A_2	1/3	30	1/8	4
A_3	1/3	300	1/8	4

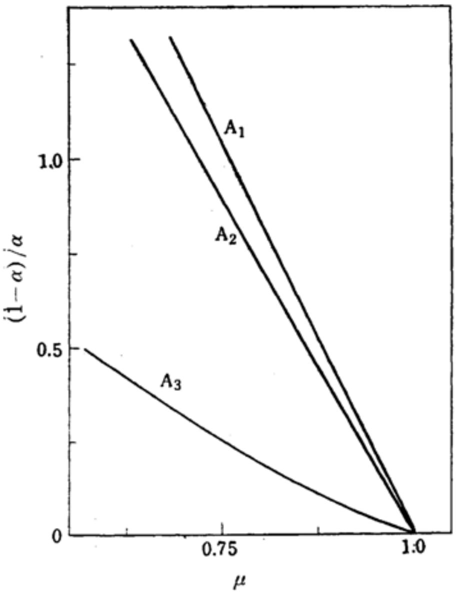

Fig. 1. Variation of $(1-\alpha)/\alpha$ with μ for the systems defined by Table I.

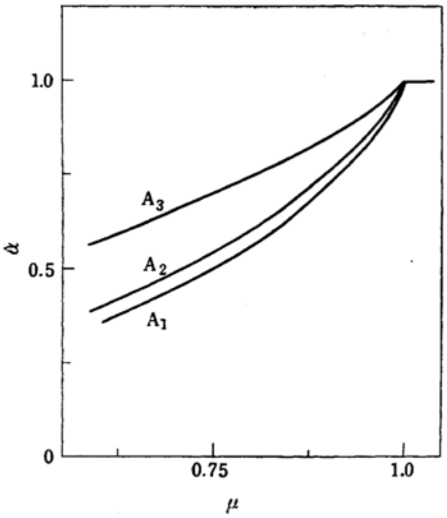

Fig. 2. Variation of α with μ for the systems defined by Table I.

TABLE II

Curve	$m_t\times10^2$	$i_t\times10^5$	$K_I^*\times10^{-4}$	$K_Y^*\times10^{-5}$	$\log\left(\frac{K_Y^*}{K_I^*}\right)$
B_1	1/3	3	1/8	1/8	1
B_2	1/3	3	1/8	10/8	2
B_3	1/3	3	1/8	100/8	3

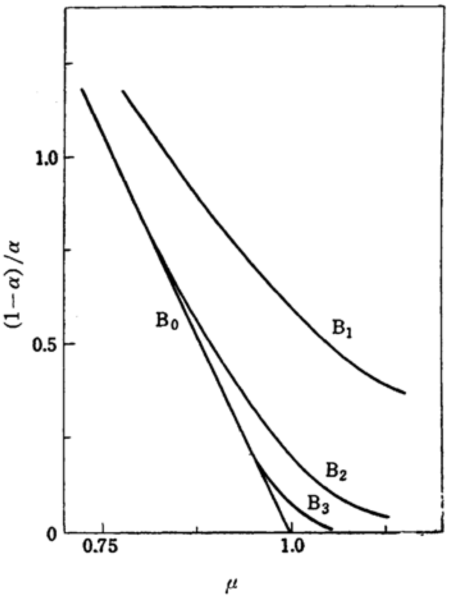

Fig. 3. Variation of $(1-\alpha)/\alpha$ with μ for the systems defined by Table II.

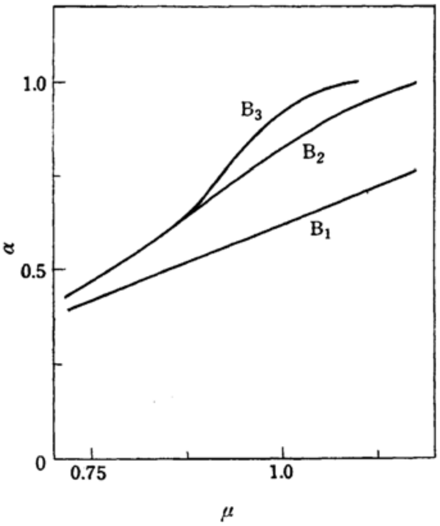

Fig. 4. Variation of α with μ for the systems defined by Table II.

molarity of the indicator was ten times smaller than $1/K_I^*$ in numero. From Fig. 3 it is seen that the deviation of the approximate equation from the general equation becomes larger as the value of $\log(K_Y^*/K_I^*)$ decreases.

In a usual plot of the titration curve (Fig. 4), the end point can be accurately determined only when $\log(K_Y^*/K_I^*)$ is larger than 4. However, if $(1-\alpha)/\alpha$ is plotted against μ (Fig. 3), the end point can be determined through extrapolation even when $\log(K_Y^*/K_I^*)$ is equal to 2 (curve B_2).

3) *Slope of the line expressed by the approximate equation.*—It is seen from Eq. 14 that the slope of the line expressed by the approximate equation is proportional to the product of m_t and K^*_{I}. Accordingly, in case of titration where Eq. 12 is well established, the apparent indicator constant can be estimated from the slope of the line expressed by this equation.

Experimental

In order to test the applicability of the linear plot described above, the following titrations were investigated:

1) Micro-titration of calcium at pH 12 using Murexide indicator, as an example of lower concentration of metal ion.

2) Titration of calcium at pH 10 using EBT indicator, as an example of lower value of K^*_{I}.

3) Titration of magnesium at pH 10 using EBT indicator, as an example of the case where value of log $(K^*_{\mathrm{Y}}/K^*_{\mathrm{I}})$ is smaller than 3.

Apparatus.—Yanagimoto Photometric Titrator Model PT-1 and Yanagimoto pH meter were used.

Reagents.—All chemicals used were the reagent grade. Standard solution of calcium was prepared by dissolving calcium carbonate (dried at 110°C), in dilute hydrochloric acid and diluting it with distilled water. Standard solution of magnesium was prepared by dissolving magnesium sulfate heptahydrate in distilled water and its concentration was gravimetrically determined with oxine[3]. Standard solution of Complexon-III was prepared by dissolving disodium ethylenediaminetetraacetate dihydrate in distilled water to produce approximately 0.01 M solution. Murexide indicator solution was prepared by shaking 40 mg. of the dye with 10 ml. of distilled water and 2 ml. of its supernatant was used. This solution was prepared daily. EBT indicator solution was prepared by dissolving 0.5 g. of Eriochrome Black T and 4.5 g. of hydroxylamine hydrochloride in 100 ml. of ethanol and its 0.5 ml. was used. This solution was stable for at least 5 months. For the adjustment of pH of the solution to 10 and 12, 1 N ammonium chloride-ammonia buffer solution and 1 N sodium hydroxide solution were used, respectively.

Procedure.—An aliquot of sample solution and a few ml. of buffer solution were placed in the titration cell and diluted to 50 ml. with distilled water. Appropriate wave-length was set and the absorbancy scale was adjusted to zero with slit. The indicator solution was pipetted into the titration cell and then titration was carried out. Absorbancies were recorded at the beginning of titration and at every 0.05 ml. of the titrant added during the titration, until the constant value of absorbancy was obtained.

Results and Discussion. — *Titration of calcium at pH 12 using Murexide indicator.* —Absorbancy measurement was made at 580 mμ. In this titration system, the values of log K^*_{Y} and log K^*_{I} are 10.5 and 5.0, respectively[4]. Although the value of log $(K^*_{\mathrm{Y}}/K^*_{\mathrm{I}})$ is sufficiently large, the photometric titration curve (Fig. 6) is somewhat round near the equivalence point, owing to the lower concentration of the calcium ion in the titration system. The plot of $(A_{S_1}-A_s)/(A_s-A_{S_{\mathrm{MI}}})$ against the volume of the titrant added (Fig. 5) gives a straight line, the intercept of which corresponds to the equivalence point. The

TABLE III

RESULTS OF PHOTOMETRIC TITRATION OF CALCIUM AT pH 12 WITH 0.01 M COMPLEXON-III USING MUREXIDE INDICATOR

Calcium taken, mg.	Titrimetric end point, ml.	Calcium found, mg.	Error %
0.50_7	1.26_6	0.50_7	0
0.50_7	1.26_6	0.50_7	0
1.01_8	2.54_0	1.01_8	0
1.01_8	2.54_0	1.01_8	0
1.28_7	3.16_0	1.26_7	−1.6
1.28_7	3.18_5	1.27_6	−0.7

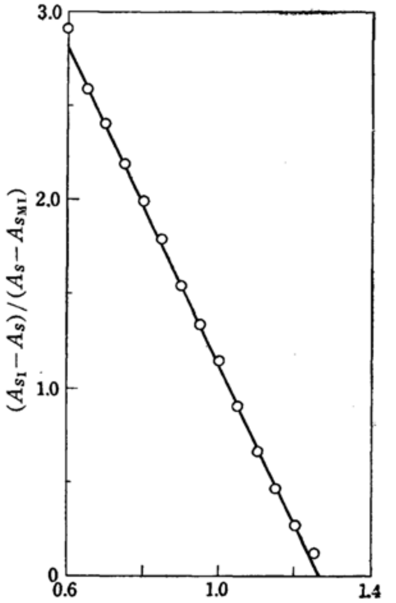

Fig. 5. Plot for titration of 0.50_7 mg. of calcium at pH 12 with Complexon-III using Murexide indicator.

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3) F. P. Treadwell and W. T. Hall, "Analytical Chemistry", Vol. II, (9th ed.), John Wiley and Sons, New York, (1942) p. 259.

4) G. Schwarzenbach, "Die komplexometrische Titration", Ferdinand Enke Verlag, Stuttgart, (1956) pp. 7, 31 and 36.

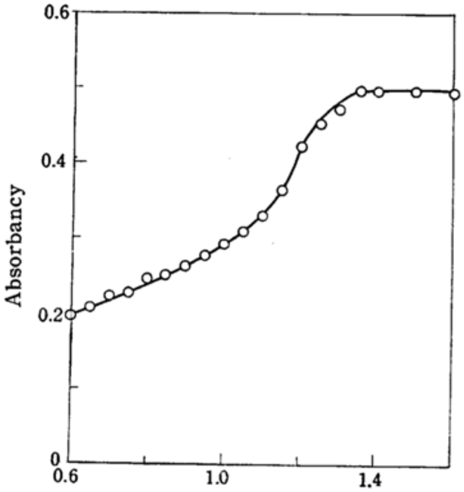

Fig. 6. Titration curve of the same titration as in Fig. 5.

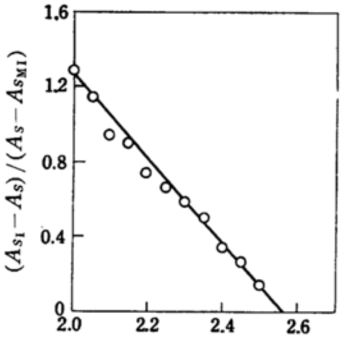

Fig. 7. Plot for titration of 1.01_8 mg. of calcium at pH 10 with Complexon-III using EBT indicator.

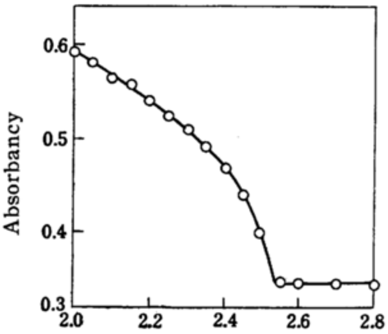

Fig. 8. Titration curve of the same titration as in Fig. 7.

results given in Table III show that the titration can be carried out with high precision.

Titration of calcium at pH 10 using EBT indicator. — In this titration system, the values of log K_Y^* and log K_I^* are 10.2 and 4.03, respectively⁴⁾. Visual titration of this system fails owing to the ambiguous color change at the end point. Even by a photometric technique, the titration curve at 545 mμ (Fig. 8) does not give a sharp end point since the value of log K_I^* is too small. However, the plot of $(As_I - A_s)/(A_s - As_{MI})$ against the volume of the titrant added (Fig. 7) gives a straight line, the intercept on the V-axis representing the equivalence point. The results given in Table IV show that precisions of the order of a few tenths of one per cent were obtained in most instances.

Titration of magnesium at pH 10 using EBT indicator. — In this titration system, the values of log K_Y^* and log K_I^* are 8.5 and 5.44, respectively⁴⁾. The value of log (K_Y^*/K_I^*) is about 3, so that the photometric titration curve at 545 mμ (Fig. 2 in the previous communication²⁾) shows some rounding near the equivalence point. However, the plot of $(As_I - A_s)/(A_s - As_{MI})$ against the volume of the titrant added gives a straight line, the intercept on the V-axis representing the equivalence point (Fig. 1 in the previous communication²⁾). The results (Table I in the previous communication²⁾) show that the titration was carried out with precision of about 1%.

TABLE IV

RESULTS OF PHOTOMETRIC TITRATION OF CALCIUM AT pH 10 WITH 0.01 M COMPLEXON-III USING EBT INDICATOR

Calcium taken, mg.	Titrimetric end point, ml.	Calcium found, mg.	Error %
1.01_8	2.55_2	1.02_3	+0.5
1.01_8	2.53_0	1.01_4	−0.4
1.01_8	2.55_2	1.02_3	+0.5
1.01_8	2.55_0	1.02_2	+0.4

Apparent indicator constant.—It was previously pointed out that the apparent indicator constant would be estimated from the slope of the linear plot of $(As_I - A_s)/(A_s - As_{MI})$ against the volume of titrant added. The values of log K_I^* obtained in the above titrations are given in Table V and compared with those described by Schwarzenbach⁴⁾(given in the fifth column in Table V). It is seen that there are considerable discrepancies between them. These discrepancies may be due to the differences in ionic strength and temperature and also to some unknown factor such as the influence of buffer components in the equilibria.

TABLE V
VALUES OF LOGARITHM OF APPARENT INDICATOR CONSTANT FOR CALCIUM AND MAGNESIUM

Metal ion	pH	Indicator	$\log K_{\mathrm{I}}^{*}$	
			Values obtained	Values reported
Calcium (II)	12	Murexide	4.3_9	5.0
Calcium (II)	10	EBT	4.0_3	3.84
Magnesium (II)	10	EBT	5.2_8	5.44

Determination of calcium and magnesium in their mixture.—Total amount of calcium and magnesium in their mixture was titrated at pH 10 with standard Complexon-III solution using EBT indicator. Absorbancy measurements were made at 545 mμ. with another aliquot of the sample solution, magnesium was masked by sodium hydroxide and calcium was titrated at pH 12 using Murexide indicator. Absorbancy measurements were made at 580 mμ. The amount of magnesium was calculated by their differences. The linear plots obtained in the titrations of total calcium and magnesium and of calcium give the same pictures as obtained in 3 and 1, respectively. The results are tabulated in Table VI.

TABLE VI
RESULTS OF TITRATION OF CALCIUM AND MAGNESIUM IN THEIR MIXTURE WITH 0.01 M COMPLEXON-III

Calcium, γ			Magnesium, γ		
taken	found[a]	deviation	taken	found[b]	deviation
513	507	−2	254	256	+2
203	203	0	254	249	−5
203	203	0	508	507	−1

a) Each value is the average of three separate determinations.

b) Each value was calculated from the difference between the average of the volume of titrant for total and that for calcium in three separate titrations.

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