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Relationship between the Color Transition and the Equivalence Point of Methylrosaniline Chloride in Non-aqueous Titration

SHIGERU YOSHIDA,* KAYOKO ODA, and SHINGO HIROSE

Kyoto College of Pharmacy, Nakauchicho 5, Misasagi, Yamashina-ku, Kyoto, 607, Japan

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The determination of some weak bases at low concentrations was investigated photometrically in non-aqueous solvents. To ensure accuracy, the chemical stoichiometric relationship between color transition of the indicator and the equivalence point was considered. The color transition of the indicator was calculated by complementary tristimulus colorimetry, which is preferable to ordinary colorimetry when dealing with several species in solution. Theoretical titration curves of titration ratio *versus* color transition were drawn and compared with the experimental data.

It was found that 10^{-2} M—10^{-4} M sample solution could be determined in non-aqueous solvents.

Keywords——chemical equilibrium; stoichiometric relationship; non-aqueous titration; colorimetry; barbital sodium; phenobarbital sodium

Non-aqueous titrations have become of considerable importance in pharmaceutical analysis[1] and have been accepted as official analytical methods in modern pharmacopoeias. In these titrations, the end-point of a titration may be determined by potential measurement during the course of the titration or by measurement of the color change of an indicator near the equivalence point.

The principle of potentiometric titration in non-aqueous media is the same as in aqueous solution, and a glass electrode is widely used as an indicator electrode. However, in non-aqueous media, these electrodes show certain undesirable features. For example, they tend to behave variably and their behavior depends on the nature and extent of pretreatment of the electrodes.[2] In addition, detection of the end-point is impossible potentiometrically in dilute sample solutions ($>10^{-2}$ M).[3]

The aim of the present work was to demonstrate the possibility of photometric determination in non-aqueous solvents by using an indicator at comparatively low concentrations of the sample (10^{-4} M order) and to determine some conditional stability constants of titrant-sample and titrant-indicator complexes for the correction of theoretical titration errors.

An indicator having its color change region as close to the equivalence point as possible is usually chosen. In non-aqueous solvents some indicators have no simple color change but pass successively through a wide range of color shades. Therefore the color transition near the equivalence point is affected by the conditions of titration, and in order to avoid indicator error, especially in dilute solution, the color transtion at the equivalence point must be known accurately.

However, it is difficult to evaluate the precise color transition over a wide range of color shades from experimental results, so in the present work the color transition near the equivalence point in non-aqueous solvents was calculated by complementary tristimulus colorimetry[4] (CTS method) which is better able to represent the character of several species than ordinary colorimetry.

The conditional stability constants were also determined by the CTS method and the equilibria of the titration system in acetic acid are discussed stoichiometrically.

As typical models, barbital sodium and phenobarbital sodium at various concentrations in anhydrous acetic acid were determined with methylrosaniline chloride (Crystal Violet) as an indicator and perchloric acid as a titrant.

Theoretical

Determination of a Weak Base

In the present theoretical treatment, titration reactions between a titrant HX (perchloric acid) and sample B (a weak base) in the presence of an indicator I (Crystal Violet) in anhydrous acetic acid as a non-aqueous solvent are discussed.

When a dilute sample solution is titrated photometrically, the consumption of HX by the indicator cannot be neglected, and the following chemical equilibria are established.

$$\mathrm{HX} + \mathrm{B} \rightleftarrows \mathrm{BH^+X^-}$$

$$\mathrm{HX} + \mathrm{I} \rightleftarrows \mathrm{IH^+X^-}$$

The quantitative expressions for these equilibria are given by the conditional stability constants, $K_{\mathrm{BH^+X^-}}$ and $K_{\mathrm{IH^+X^-}}$ defined by

$$K_{\mathrm{BH^+X^-}} = \frac{[\mathrm{BH^+X^-}]}{[\mathrm{HX}][\mathrm{B}]} \tag{1}$$

$$K_{\mathrm{IH^+X^-}} = \frac{[\mathrm{IH^+X^-}]}{[\mathrm{HX}][\mathrm{I}]} \tag{2}$$

Where [HX], [B], *etc.* denote the molar concentrations of HX, B, *etc.*, respectively. In these equations the activity of acetic acid is omitted since the activity of the solvent may be considered constant in dilute solution. In a titration procedure, the following stoichiometric relationships hold throughout the titration:

$$C_{\mathrm{HX}} = [\mathrm{HX}] + [\mathrm{BH^+X^-}] + [\mathrm{IH^+X^-}] \tag{3}$$

$$C_{\mathrm{B}} = [\mathrm{B}] + [\mathrm{BH^+X^-}] \tag{4}$$

$$C_{\mathrm{I}} = [\mathrm{I}] + [\mathrm{IH^+X^-}] \tag{5}$$

where C_{HX}, C_{B} and C_{I} refer to the total molar concentrations of the acid HX, base B and indicator I, respectively. The color transition ϕ[5] which is determined from absorption spectra by the CTS method is defined as

$$\phi = \frac{[\mathrm{I}]}{C_{\mathrm{I}}} \tag{6}$$

Combining Eqs. (2) and (6), and Eqs. (5) and (6), we obtain the following equations for [HX] and [IHX].

$$[\mathrm{HX}] = \frac{1}{K_{\mathrm{IH^+X^-}}}\frac{1-\phi}{\phi} \tag{7}$$

$$[\mathrm{IH^+X^-}] = (1-\phi)C_{\mathrm{I}} \tag{8}$$

Substituting Eqs. (7) and (8) into Eq. (3), we have

$$[\mathrm{BH^+X^-}] = C_{\mathrm{HX}} - \frac{1}{K_{\mathrm{IH^+X^-}}}\frac{1-\phi}{\phi} - (1-\phi)C_{\mathrm{I}} \tag{9}$$

From Eqs. (1), (2) and (9), we get

$$[\mathrm{B}] = \frac{K_{\mathrm{IH^+X^-}}}{K_{\mathrm{BH^+X^-}}}\frac{\phi}{1-\phi}\left\{C_{\mathrm{HX}} - \frac{1}{K_{\mathrm{IH^+X^-}}}\frac{1-\phi}{\phi} - (1-\phi)C_{\mathrm{I}}\right\} \tag{10}$$

Sample concentration C_{B} is obtained by substitution into Eq. (4) from Eqs. (7), (8), (9) and (10)

$$C_{\mathrm{B}} = \left(\frac{K_{\mathrm{IH^+X^-}}}{K_{\mathrm{BH^+X^-}}}\frac{\phi}{1-\phi} + 1\right)\left\{C_{\mathrm{HX}} - \frac{1}{K_{\mathrm{IH^+X^-}}}\frac{1-\phi}{\phi} - (1-\phi)C_{\mathrm{I}}\right\} \tag{11}$$

This equation hols over the full range of titration and determination of the smaple is theoretically possible after calculation of the color transition.

In the case of an ordinary sample with which the effect of indicator may be neglected, the term concerned with the amount of indicator may be omitted, and equation (11) can be simplified and rewritten as follows:

$$C_{\mathrm{B}} = \left(\frac{K_{\mathrm{IH^+X^-}}}{K_{\mathrm{BH^+X^-}}}\frac{\phi}{1-\phi}+1\right)\left(C_{\mathrm{HX}}-\frac{1}{K_{\mathrm{IH^+X^-}}}\frac{1-\phi}{\phi}\right) \tag{12}$$

Derivation of $K_{\mathrm{IH^+X^-}}$ and $K_{\mathrm{BH^+X^-}}$

Equations (11) and (12) show that $K_{\mathrm{IH^+X^-}}$ and $K_{\mathrm{BH^+X^-}}$ must be known for the determination of a sample. These conditional stability constants can also be calculated by utilizing the CTS method.

$K_{\mathrm{IH^+X^-}}$ is calculated in the system containing only indicator and titrant. Under such conditions, Eq. (3) takes the form

$$C_{\mathrm{HX}} = [\mathrm{HX}] + [\mathrm{IH^+X^-}] \tag{13}$$

Substitution of Eqs (5), (6), (13) into (2) gives

$$K_{\mathrm{IH^+X^-}} = \frac{1-\phi}{\phi}\,\frac{1}{C_{\mathrm{HX}}-(1-\phi)C_{\mathrm{I}}} \tag{14}$$

The calculation of $K_{\mathrm{IH^+X^-}}$ may be based on Eq. (14) and the definitions of C_{I} and C_{HX}.

$K_{\mathrm{BH^+X^-}}$ cannot be calculated directly in the system containing B, HX and their complex, because the shape of the absorption spectrum of B in the ultraviolet region does not change compared with that of $\mathrm{BH^+X^-}$ as a result of the formation of the complex. Thus, in order to determine $K_{\mathrm{BH^+X^-}}$, the color transition and stoichiometric relationships between sample, titrant and indicator are used. Substitution of Eq. (9) in Eq. (4) gives

$$[\mathrm{B}] = C_{\mathrm{B}} - C_{\mathrm{HX}} + \frac{1-\phi}{\phi}\left(\phi C_{\mathrm{I}}+\frac{1}{K_{\mathrm{IH^+X^-}}}\right) \tag{15}$$

Substituting Eqs. (7), (9) and (15) into Eq. (1), we have

$$K_{\mathrm{BH^+X^-}} = K_{\mathrm{IH^+X^-}}\frac{\phi}{1-\phi}\left\{\frac{C_{\mathrm{B}}}{C_{\mathrm{HX}}-(1-\phi)\left(C_{\mathrm{I}}+\dfrac{1}{\phi K_{\mathrm{IH^+X^-}}}\right)}-1\right\}^{-1} \tag{16}$$

Eq. (16) shows that $K_{\mathrm{BH^+X^-}}$ can be calculated by utilizing the definitions of C_{HX}, C_{B}, C_{I} and $K_{\mathrm{IH^+X^-}}$. Eq. (16) holds for any ratio $C_{\mathrm{HX}}/C_{\mathrm{B}}$, but it is very complicated. By assuming that [HX] may be neglected in Eq. (3) before the equivalence point, Eq. (16) can be simplified to Eq. (17).

$$K_{\mathrm{BH^+X^-}} = K_{\mathrm{IH^+X^-}}\frac{\phi}{1-\phi}\left\{\frac{C_{\mathrm{B}}}{C_{\mathrm{HX}}-(1-\phi)C_{\mathrm{I}}}-1\right\}^{-1} \tag{17}$$

Calculation of Color Transition by the Complementary Tristimulus Colorimetry

In the CTS method, absorption spectra are divided into three portions so as to better represent the absorptive properties, and the portions are named the *u*, *v* and *w* ranges. A series of absorbances (on a chart) is measured at a regular wavelength interval in each of three ranges and the sums of the absorbances are represented by *Ru*, *Rv* and *Rw*, respectively; their total is *J*

$$Rr = \sum_{i=1}^{n} Ari \quad (r=u,v,w) \tag{18}$$

$$J = Ru + Rv + Rw = E\cdot c\cdot l \tag{19}$$

Here *Ari* and *Rr* denote the *i*-th absorbance reading in the *r* range and the sum, respectively. *E*, which may be called the overall absorptivity, is related to the equivalent parameter ε (extinction coefficient) in Lambert–Beer's law. *C* is the analytical concentration of the colorant in the absorbing solution, expressed in a suitable unit and *l* is the length of the light path.

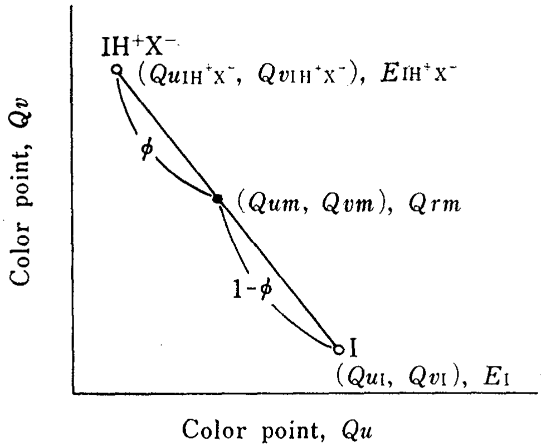

Fig. 1. Qu–Qv Plot for the I and IH^+X^- System

E_I, $E_{IH^+X^-}$: Overall absorptivities of base and acid forms of indicator.
(Q_{uI}, Q_{vI}): Coordinates of color point of basic indicator form.
($Q_{uIH^+X^-}$, $Q_{vIH^+X^-}$): Coordinates of color point of acidic indicator form.
Qrm: Color point of the mixture, I and IH^+X^-

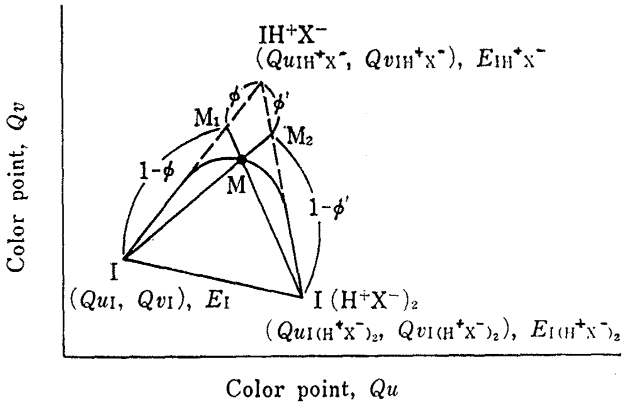

Fig. 2. Qu–Qv Plot of Ternary Colorant System

$\phi=\frac{[I]}{[I]+[IH^+X^-]}$, $\phi'=\frac{[I(H^+X^-)_2]}{[I(H^+X^-)_2]+[IH^+X^-]}$
$Q_{rIH^+X^-}$ was determined by extrapolation and $E_{IH^+X^-}$ was calculated from Eqs. (22)—(24).

Qu, Qv and Qw correspond to Ru/J, Rv/J and Rw/J, respectively, and Qr, which is the generic notation for Qu, Qv and Qw, represents the complementary color point and is independent of the concentration of the colorant.

$$Qr=\frac{Rr}{J} \tag{20}$$

If two kinds of colorants I and IH^+X^- are formed in a titration, the Qr plot near the equivalence point appears in a graph in which two kinds of Qr among the three are coordinates as a straight line which connects two fixed points Qr_I and $Qr_{IH^+X^-}$ (Fig. 1). In Fig. 1, Qr_I and $Qr_{IH^+X^-}$ are Qr for the pure colorants I and IH^+X^-.

A color transition of the indicator corresponding to Qrm which exists on the linear Qr plot is calculated from the equation containing E_I, $E_{IH^+X^-}$, Qr_I and $Qr_{IH^+X^-}$ as follows:

$$\phi=\frac{E_{IH^+X^-}(Qr_{IH^+X^-}-Qrm)}{E_I(Qrm-Qr_I)+E_{IH^+X^-}(Qr_{IH^+X^-}-Qrm)} \tag{21}$$

where E_I, $E_{IH^+X^-}$ and Qr_I, $Qr_{IH^+X^-}$ are constants previously established from the absorption spectra; the former two are E of I and IH^+X^-, the latter two are Qr of each colorant.

In the three colorant system (I, IH^+X^-, and $I(H^+X^-)_2$), three Qr corresponding to each colorant are represented, but in the successive formation system, IH^+X^- cannot be satisfactorily separated. Qr of IH^+X^- can be obtained graphically as shown Fig. 2, but E of IH^+X^- cannot. However, Hirose *et al.*⁶⁾ obtained it by calculation from the following equations by substituting the values of Qr_I, $Qr_{IH^+X^-}$ and E_I into them.

$$Rum=Q_{uI}E_I[I]+Q_{uIH^+X^-}E_{IH^+X^-}[IH^+X^-] \tag{22}$$

$$Rvm=Q_{vI}E_I[I]+Q_{vIH^+X^-}E_{IH^+X^-}[IH^+X^-] \tag{23}$$

$$Rwm=Q_{wI}E_I[I]+Q_{wIH^+X^-}E_{JH^+X^-}[IH^+X^-] \tag{24}$$

Rum, Rvm and Rwm represent the sum of the absorbances of the mixture of I and IH^+X^- in the u, v and w ranges, respectively. By resolving the equations from Eq. (22) to (24), [I], $[IH^+X^-]$ and $E_{IH^+X^-}$ at point M can be determined simultaneously.

Points M_1 and M_2 graphically define straight lines to opposite sides from apex I or $I(H^+X^-)_2$ and show the color transition of the indicator as follows.

$$[IH^+X^-] : [I] = \phi : 1-\phi \tag{25}$$

$$[IH^+X^-] : [I(H^+X^-)_2] = \phi' : 1-\phi' \tag{26}$$

Thus the proportion of indicator species at point M is

$$[IH^+X^-] : [I] : [I(H^+X^-)_2] = \phi\phi' : (1-\phi)\phi' : (1-\phi')\phi \tag{27}$$

Experimental

Apparatus——The photometric determination was carried out with a Shimadzu MPS-50L spectrophotometer. Titrant was added with a Metrohm piston buret (capacity, 5 ml).

Materials——Anhydrous Acetic Acid: Glacial acetic acid was freed from water by repeated distillation.

Perchloric Acid Solution in Anhydrous Acetic Acid, 0.1 M: Dissolve 8.5 ml of perchloric acid (70—72%) in anhydrous acetic acid, add 22.2 ml of acetic anhydride and make the volume up to 1000 ml with the same solvent. Standardize against potassium hydrogen phthalate and dilute as required.

Crystal Violet (Hexamethylpararosaniline Chloride), 10^{-3} M: Recrystallize twice from acetone–ethyl acetate 2: 1, weigh accurately about 44.4 mg of Crystal Violet (previously dried at 100° for two hours) and dissolve in 100 ml of anhydrous acetic acid in a volumetric flask.

All other weak basic samples were of pharmacopoeia or analytical grade and were prepared as solutions of 10^{-1} M—10^{-3} M.

Procedure of Determination——All analytical procedures were performed in an air-conditioned room at 20±1°.

A sample solution of 1 ml (10^{-1} M—10^{-3} M) was placed in a 10 ml volumetric flask, and 0.05 ml of 10^{-3} M Crystal Violet was added with a piston buret. The mixture was titrated with 10^{-1}—10^{-3} M perchloric acid (corresponding to the sample concentration) from the piston buret, with gentle stirring. When the initial violet color changed from blue to green, the titration was stopped at any color shade of that color and the solution was made up to the marked line with acetic acid. The absorption spectrum in the visible region was measured in a 1 cm quartz cell against anhydrous acetic acid as a reference, and the three ranges for the CTS method were selected (*u*, *v* and *w* ranges). From the sum of ten absorbance readings in each range, the color point and color transition were calculating by using Eqs. (19), (20) and (21). The use of Eq. (11) or (12) for determination of the sample concentration is a little troublesome, so a personal computer (Yokogawa Hewlett Packard M-10) was used for the rapid computation of results.

Procedure for $K_{IH^+X^-}$ Calculation——A known amount of $HClO_4$ was added to a solution containing 0.05 ml of 10^{-3} M Crystal Violet in a 10 ml volumetric flask, to give the desired molar ratio of $HClO_4$ to Crystal Violet and the solution was diluted to the mark. Absorption spectra of solutions of various molar ratios were obtained. From the CTS parameters in the same three ranges, it is possible to calculate the constant by the use of Eqs. (14) and (21).

Procedure for $K_{BH^+X^-}$ Calculation——A known amount of 10^{-1} M $HClO_4$ was added to a solution containing 1 ml of 10^{-1} M basic sample solution and 0.05 ml of 10^{-3} M Crystal Violet in a 10 ml flask. The procedure was similar to that described above for $K_{IH^+X^-}$ calculation.

Results and Discussion

Chemical Species of Crystal Violet

Usually, indicators for visual titration have successive color changes near the end point. Crystal Violet, which is frequently used as an indicator for non-aqueous titration, changes near the end point successively from violte~blue-green~green-blue~green~green-yellow, and eventually to yellow. The CTS method was applied to investigate the species of indicator formed in the process of titration. Absorption spectra of solutions containing different molar ratios of perchloric acid and a constant concentration of Crystal Violet were measured in the visible region and are shown in Fig. 3. In Fig. 3, with increase of the molar ratio C_{HX}/C_I, the absorption bands near 580 nm first shift to longer wavelength and then shift back to shorter wavelength again. This suggests the formation of several chemical species of indicator. For the effective application of the CTS method, three specific wavelength bands should be selected, and 415—460 nm, 550—595 nm and 600—645 nm were selected as *u*, *v* and *w* ranges, respectively. In these ranges, the absorption curves changed markedly with change of the molar ratio.

Various CTS parameter were calculated from Eqs. (18) and (20), and are listed in Table I. A *Qu*—*Qw* plot is shown Fig. 4. By extrapolation of the plot in Fig. 4, a triangular shape is

Table I. CTS Parameters of Crystal Violet

	Rr			*J*	*Qr*		
	Ru	*Rv*	*Rw*		*Qu*	*Qv*	*Qw*
(1)[a]	1.09	135.23	50.53	186.85	0.006	0.724	0.270
(2)	1.21	127.53	51.14	179.88	0.007	0.709	0.284
(3)	5.80	100.23	63.84	169.87	0.034	0.590	0.376
(4)	11.56	72.59	72.98	157.13	0.074	0.462	0.464
(5)	16.21	48.40	70.59	135.20	0.120	0.358	0.522
(6)	21.38	34.70	64.85	120.93	0.177	0.287	0.536
(7)	25.34	23.29	52.73	101.36	0.250	0.230	0.520
(8)	29.78	14.59	37.76	82.13	0.363	0.178	0.460
(9)	35.39	4.90	13.97	54.26	0.652	0.090	0.257
(10)	39.30	1.13	1.62	42.05	0.935	0.027	0.039

[a] (1), (2), ------ correspond to the numbers in Fig. 3.

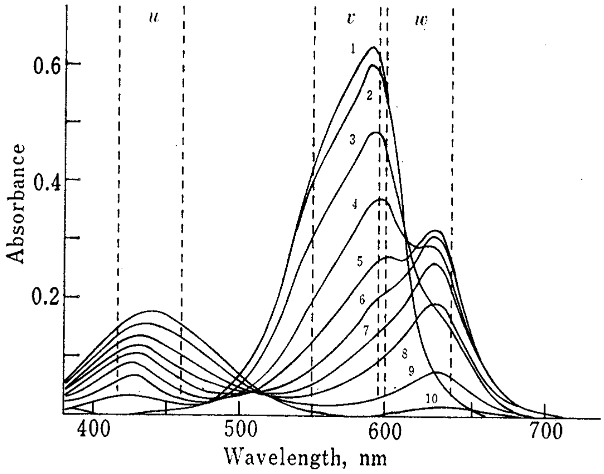

Fig. 3. Absorption Spectra of Crystal Violet titrated with $HClO_4$ in Acetic Acid

Crystal Violet: 5×10^{-6} M.

Molar ratio (C_{HX}/C_I) 1: 0, 2: 3.0, 3: 3.5, 4: 4.0, 5: 5.0, 6: 7.0, 7: 8.0, 8: 10.0, 9: 18.0, 10: 75.0.

C_{HX} and C_I are the total concentrations of perchloric acid and Crystal Violet, respectively.

Ranges *u*, *v* and *w* are 415—460 nm, 550—595 nm and 600—645 nm, respectively, for calculation of the CTS parameters.

obtained, and *Qr* points should fall on the lines or inside the triangle. From the definition of the CTS method, chemical species of *Qr* which are on the straight line are mixtures of the two pure colorants corresponding to the ends of the line. For *Qr* points inside the triangular shape, the chemical species are mixtures of three pure colorants. The complicated color change near the end point is due to variations of the molar ratio of the three pure colorants (violet, green and yellow). It has become apparent that these species correspond to complex I (violet), I ($HClO_4$) (green) and I $(HClO_4)_2$ (yellow) on the basis of the CTS method. The molar ratio of color mixture which is present at a particular point M can be obtained from Eqs. (25), (26) and (27).

The choice of a suitable indicator for the titration of weak acids and bases is still largely a matter of experience. However, stoichiometric relationships of indicator species determined by the CTS method may provide a theoretical basis for choosing a suitable indicator.

Theoretical Titration Curve

Below 10^{-3} M sample, indicator error cannot be ignored and the end point cannot be accurately determined. Even in such a case, however, it is possible to determine the sample concentration by a consideration of the stoichiometric relationships of chemical species contained in the solution, and calculation of the color transition from absorption spectra during the titration process can play an important role in minimizing the indicator error. Thus far, the color transition has been treated as a variable in the theoretical analysis and has not been obtained consecutively in the titration process, but by using the color point obtained by the CTS method, it may be calculated readily from the experimental data.

The agreement between the theoretical and found values was next investigated. The

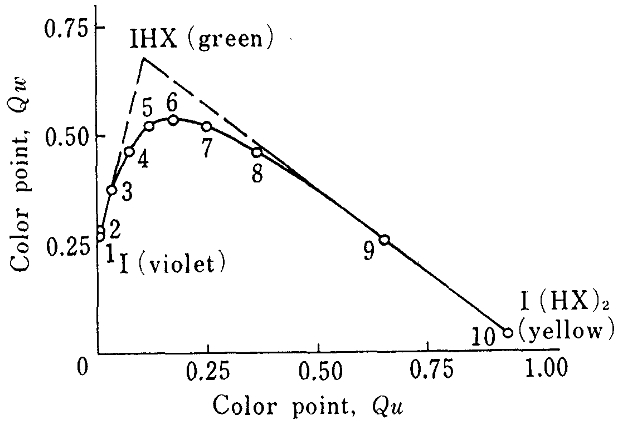

Fig. 4. *Qu–Qw* Plot for Crystal Violet titrated with $HClO_4$

Crystal Violet: 5×10^{-6} M
Molar ratio (C_{HX}/C_I) 1: 0, 2: 3.0, 3: 3.5, 4: 4.0, 5: 5.0, 6: 7.0, 7: 8.0, 8: 10.0, 9: 18.0, 10: 75.0.

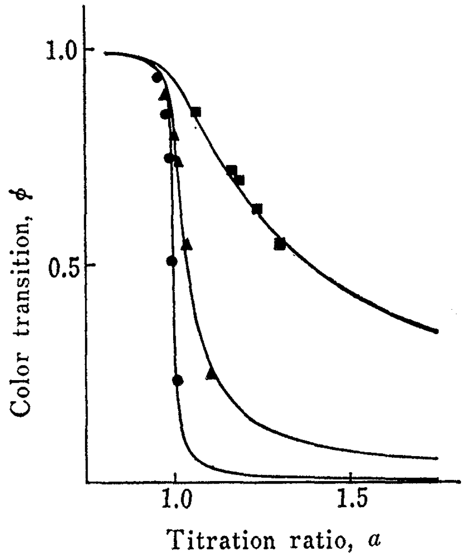

Fig. 5. Theoretical Titration Curve and Experimental Results for Barbital Sodium

——: theoretical curve, ●: experimental data for 10^{-2} M sample solution, ▲: 10^{-3} M., ■: 10^{-4} M.
$K_{IH^+X^-}=2.7\times10^4$, $K_{BH^+X^-}=1.1\times10^7$.
Titrant: 10^{-2}—10^{-4} M $HClO_4$.
Indicator: 5×10^{-6} M Crystal Violet.

theoretical relationship of titration ratio and color transition is obtained by modification of Eq. (11) as below.

$$C_{HX} = C_B\left(\frac{K_{IH^+X^-}}{K_{BH^+X^-}}\frac{\phi}{1-\phi}+1\right)^{-1} + \frac{1}{K_{IH^+X^-}}\frac{1-\phi}{\phi} + (1-\phi)C_I \tag{28}$$

By defining the titration ratio a as C_{HX}/C_B, we have Eq. (29).

$$a \equiv \frac{C_{HX}}{C_B} = \left\{\frac{K_{IH^+X^-}}{K_{BH^+X^-}}\frac{\phi}{1-\phi}+1\right\}^{-1} + (1-\phi)\left(\frac{1}{K_{IH^+X^-}\phi} + C_I\right)C_B^{-1} \tag{29}$$

Eq. (29) holds throughout the titration process and shows the theoretical a-ϕ relation. Theoretical titration curves for 10^{-2}—10^{-4} M barbital sodium (C_B) based of the $K_{IH^+X^-}$ and $K_{BH^+X^-}$ values in Table II are shown as full lines in Fig. 5, together with experimental data for a and ϕ. The theoretical curves agree very closely with the experimental results.

Thus, it may be concluded that Eq. (11) is suitable for the determination of dilute and weak basic sample solutions and that the equivalence point can be estimated from any point where the color change of the indicator begins.

Conditional Stability Constant

Conditional stability constants for complexes of basic samples with $HClO_4$ in acetic acid were calculated from Eqs. (14) and (17), and are listed in Table II. Conditional stability constants of complexes of Crystal Violet-$HClO_4$ are comparative small, which accounts for the slow movement of *Qr* with a large variation of molar ratio C_I/C_{HX} (Fig. 4). This is responsible for the uncertainty regarding the end point. Accordingly, Crystal Violet should be chosen under experimental conditions in which the end point corresponds to the color change from violet to green, not from green to yellow.

Results of Determination

Determinations using, for example, barbital sodium and phenobarbital sodium were attemped, and the results are listed in Table III. Barbital sodium of 2.062—0.010_3 mg/ml,

TABLE II. Conditional Stability Constants of the Complexes with Perchloric Acid

Crystal Violet $K_{IH^+X^-}$	Barbital sodium $K_{BH^+X^-}$	Phenobarbital sodium $K_{BH^+X^-}$
2.7×10^4	1.1×10^7	4.2×10^6

Ea: 3737×10^4, Eb: 2565×10^4
Qua: 0.006, Qva: 0.724, Qwa: 0.270
Qub: 0.108, Qvb: 0.214, Qwb: 0.678
Qrb values were obtained by extrapolation (Fig. 4).

TABLE III. Determinations of Barbital Sodium and Phenobarbital Sodium

	Taken (mg/ml)	Found (mg/ml)	Purity (%)
Barbital sodium	2.062	2.058 (0.002)[a]	99.8
	0.206_2	0.204_5 (0.003)	99.1_8
	0.020_6	0.020_3 (0.004)	98.5_4
	0.010_3	0.009_9 (0.002)	96.1_2
Phenobarbital sodium	2.542	2.533 (0.002)	99.6
	0.254_2	0.252_0 (0.002)	99.1_3
	0.025_4	0.024_8 (0.003)	97.6_4

a) Standard deviation.

and phenobarbital sodium of 2.542—0.025_4 mg/ml correspond to 10^{-2} M—5×10^{-5} M and to 10^{-2} M —10^{-4} M solutions. Eq. (12), which neglects the indicator concentration, was used in the cases of 10^{-2} M and 10^{-3} M sample, and Eq. (11) was used for more dilute solutions. The results (Table III) for phenobarbital sodium vary somewhat more than those for barbital sodium because the conditional stability constant of phenobarbital sodium is less than that of barbital sodium (Table II).

The experimental error of determination at 10^{-5} M order of concentration became relatively large, since the sample concentration was approaching that of the indicator (5×10^{-6} M).

These results indicate that dilute sample solutions in non-aqueous solvents may be determined accurately by this procedure.

Simplified CTS Method

In order to avoid the need for absorbance reading in the three ranges, the absorbances at 430 nm, 590 nm and 635 nm, which are representative of the *u*, *v* and *w* ranges, were used. Accordingly, Eqs. (19) and (20) can be rewritten as follows.

$$J = Au + Av + Aw \tag{30}$$

$$Qr = \frac{Ar}{\sum_{r}^{u,v,w} Ar} \tag{31}$$

The results obtained from these equations were in good accord with those obtained by the ordinary CTS method.

References and Notes

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