

Complexometric Titration using a Tensammetric Wave of Organic Reagents as an End-point Detection

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A new method for the end-point detection in complexometric titration using a tensammetric wave of various organic reagents was studied. A tensammetric wave of these organic reagents having conjugated double bonds shows a high sensitivity as compared with the common a.c. polarographic wave. Its wave disappears by the chelate formation of organic reagent with the metal ion and reappears by the liberation of the reagent with the exchange reaction between the metal-reagent complex and a chelating agent such as EDTA. Therefore, when a small amount of these reagent as a tensammetric indicator is added before the titration, a tensammetric wave which corresponds to the liberated indicator appears at the equivalence point of the metal ion. In this study, adsorption behaviors of organic reagents, such as oxines, alizarin complexone, phthalein complexone derivatives and sulfophthalein complexone derivatives, onto the mercury surface has been studied both by the measurements of the electrocapillary curve and a.c. polarographic method. A typical Langmuir type relation was established between the concentration of the organic reagent and its tensammetric wave height. From the experimental results, it was considered that the molecules or ions are adsorbed to form a stable monolayer in parallel to the electrode surface at more positive potential than the electrocapillary maximum. For the practical applications, alizarin complexone and thymolphthalein complexone were suggested as the most suitable indicator for the complexometric titration in the pH range from 2 to 10. The titrimetry could be carried out satisfactorily for metals such as copper, cadmium, zinc, nickel, cobalt, manganese, lead, indium, thorium and bismuth even in the concentration less than 0.4mg/100ml with 0.001M EDTA within 1.5% relative error by this method.

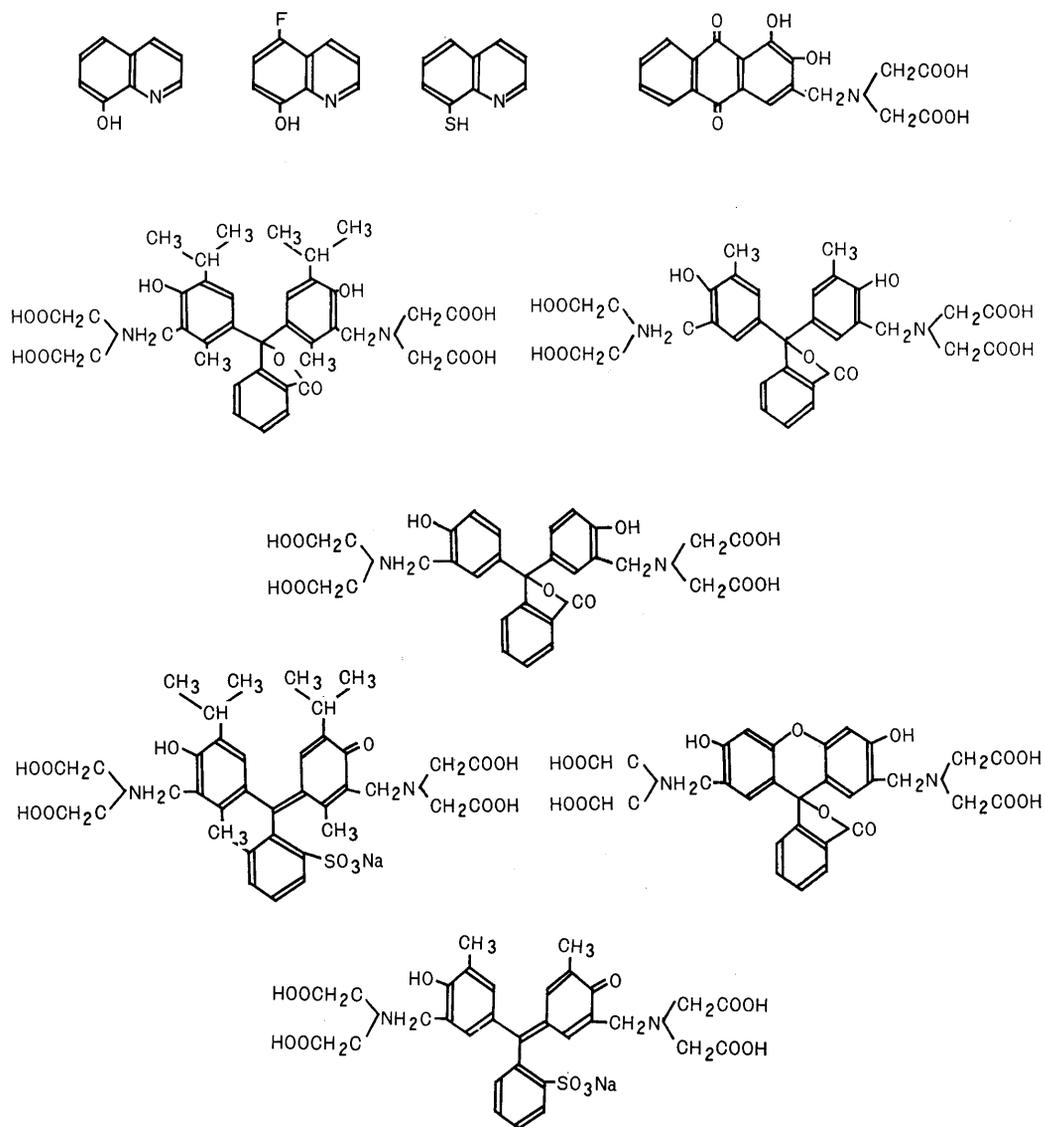
Introduction

In the previous papers, the potentiometric titration of metals with EDTA using the metal¹⁾ and metal oxide²⁾ indicator electrodes has been reported. In the successful complexometric titration of metals with an amperometric end-point detections, end-point is usually determined by measuring the variation of limiting diffusion current of metal or

titrant. In a.c. polarography, the wave caused by the adsorption of the surfactant at the mercury solution interface is called tensammetric wave,³⁾ which does not involve the oxidation-reduction reaction at the electrode surface. Its wave is very sensitive to the surfactant concentration as compared with the common a.c. polarographic wave.

Fujinaga and his co-workers⁴⁾ studied the tensammetric wave of oxines and pointed out

Table 1. Various Aromatic Compounds.



that these wave are probably due to the adsorption of neutral form of oxines. When oxine is used as a titrant for a few metals such as copper and zinc, oxine reacts with these metals and the tensammetric wave of an excess oxine appears after the equivalence point of these metals.

The tensammetric wave of the organic indicators utilized here disappears by the chelate formation of organic indicators with metals and reappears by the liberation of the indicator with the exchange reaction between the metal-indicator complex and a chelating agent such as EDTA. Therefore, when a small amount of the indicator is added before the titration, end-point of the metal ion can be detected by remarkable increase of the tensammetric wave caused by the liberation of the indicator after the equivalence point of metal.

M.A. Gerovich⁵⁾ concluded from the study of the electrocapillary behaviors that the adsorption of aromatic compounds on a mercury surface are due to the interaction between the π -electrons of the conjugated double bonds and the positively charged mercury surface. Various workers^{6,7)} have shown by the measurements of the electro-capillary curve that aromatic compounds strongly adsorb on the mercury-electrolyte solution interface.

Various organic indicators having a conjugated double bonds, such as oxine derivatives, alizarin complexone, phthalein complexones and sulfophthalein complexones as shown in Table 1, were used. In this investigation, unknown acid dissociation constants of these indicators and stability constants of metal-indicator complex were determined, and the adsorption behaviors of these indicators were studied both by the polarographic method and the measurements of the electrocapillary curve. Subsequently, the complexometric titration of metal cations using these organic indicators as an end-point detection was investigated. Satisfactory results were obtained for the titration of various metal cations

by this method.

Acid Dissociation Constant and Stability Constant

In the theoretical consideration of the titration of metal ions using a tensammetric wave of organic indicators as an end-point detection, it is necessary to know acid dissociation constants of indicators and stability constants of metal-indicator complexes. These acid dissociation constants and the stability constants were determined by the pH titration and the spectrophotometric method.

Acid Dissociation Constants: ALC contains a couple of acetic acid groups and two phenolic hydroxyl groups in a molecule and it may acts as a tetrabasic acid. Therefore, acid dissociation constants of ALC can be determined by the pH titration. Titration was carried out with a carbonate free potassium hydroxide solution under the nitrogen atmosphere at ionic strength $\mu=0.2$. The titration curve of ALC represents sharp inflection points corresponding to the first and second stages of neutralization. (Fig. 1)

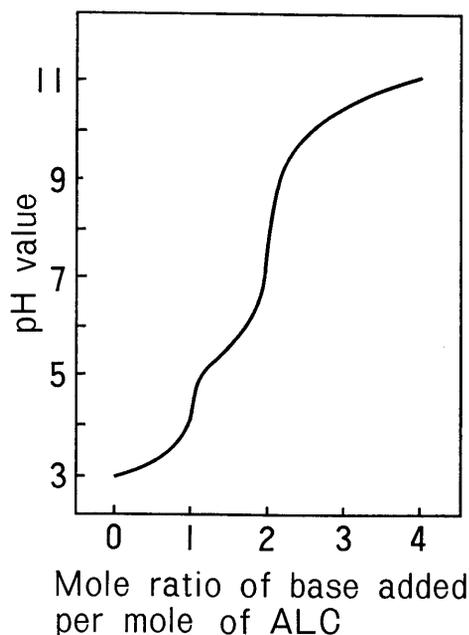


Fig. 1. Acid-base titration curve of ALC with potassium hydroxide.
Initial concentration of ALC: 0.001M
Concentration of potassium hydroxide: 0.1M

Between the first and second inflection points, it seems reasonable to assume that the dominant species of ALC are H_3I^- and H_2I^{2-} . The pk_2 value could be estimated to be 5.51 from the pH value at the half titration point of this region. The pk_1 , pk_3 and pk_4 values were then calculated by the procedure proposed by J.C. Speakman.⁸⁾ On the other hand, since maximum absorption of H_3I^- appears at 423 nm. and that of H_2I^{2-} appears at 520 nm., the second acid dissociation constant, pk_2 , of ALC can also be determined spectrophotometrically by the change of absorbance of H_3I^- or H_2I^{2-} with the variation of pH.

Phthalein complexone derivatives were not available in a pure state even by the recrystallization, so that the acid dissociation constant cannot be determined potentiometrically, while pk_5 value can be estimated spectrophotometrically⁹⁾ by the same method as that of ALC. The value of acid dissociation constants are tabulated in Table 2.

Table 2. Acid Dissociation Constant

Reagents	pk_1	pk_2	pk_3	pk_4	pk_5	pk_6
oxine	5.16	9.63 ¹³⁾				
5-fluoro-oxine	2.76	10.55 ¹³⁾				
thio-oxine	1.74	9.20 ¹¹⁾				
ALC	2.18	5.51 5.50**	10.05	11.53*		
TPC					11.84**	
PC	2.2	2.9	7.0	7.8	11.4	12.01 ¹²⁾
PPC					11.60**	
Calcein		<4	5.4	9.0	10.5	>12 ¹⁴⁾
MTB	$pk_1+pk_2+pk_3$	<4.5		7.2	11.15	13.4 ¹⁴⁾
XO	-1.09	2.58	3.23	6.37	10.46	12.28 ¹⁴⁾

* Acid-base titration method

** Spectrophotometric method

Stability Constants of Metal-ALC Complex:

The yellow form of ALC, H_3I^- , (λ_{max} 423nm.) exists in the pH range 3.5 to 4.5, but at higher pH value than 6, the intensity of this band falls off and the new band of red form of ALC, H_2I^{2-} , appears at 520nm. In the pH range 3.5 to 4.5, ALC reacts with many cations,

such as copper, zinc, nickel, cobalt and lead,

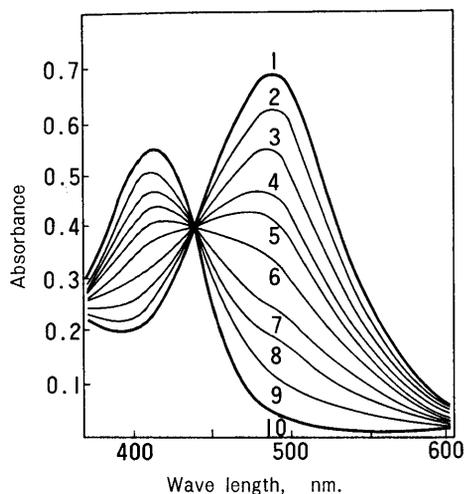


Fig. 2. Absorption spectra of ALC in the presence of excess of zinc at various pHs. ALC: $2 \times 10^{-5} M$, Zn: $4 \times 10^{-3} M$, $\mu=0.2(NaClO_4)$ Ref.: water, room temp. pH: 1=4.64, 2=3.68, 3=3.41, 4=3.24, 5=3.10, 6=2.98, 7=2.82, 8=2.68, 9=2.59, 10=2.42.

to form red colored metal chelate.¹⁰⁾ Therefore, this phenomenon can be applied to the determination of the stability constant of these metal complex. Fig. 2 shows the absorption spectra of the mixture of $2 \times 10^{-5} M$ ALC and $4 \times 10^{-3} M$ zinc at various pHs. ($\mu=0.2$)

If the composition of divalent metal complex with ALC are assumed to be only a MHI^- in the pH range 3.5 to 4.5, these complex formation reaction can be expressed to be:



The equilibrium constant, K' ,

can be expressed as follows:

$$K' = \frac{[MHI^-][H^+]^2 \alpha_{H(H_3I)}}{[M^{2+}][H_3I^-]'} = K_{MHI} \cdot k_2 \cdot k_3 \quad (2)$$

where K_{MHI} refers to the stability constant of MHI^- , and k_2 and k_3 are the acid dissociation constant of second and third step, respectively. $[H_3I^-]'$ denotes the total concentra-

tion of free ALC and is expressed as follows:

$$\begin{aligned} [H_3I^-]' &= [H_4I] + [H_3I^-] + [H_2I^{2-}] \\ &= [H_3I^-] \left\{ \frac{[H^+]}{k_1} + 1 + \frac{k_2}{[H^+]} \right\} \\ &\equiv [H_3I^-]^{\alpha_{H(H_3I)}} \end{aligned}$$

From the experimental results, neutral form of ALC, H_4I , shows no absorbance at about 500nm. but the absorbance of H_2I^{2-} appears at this wave length. However, since the second stage acid dissociation constant is to be 5.51, the presence of H_2I^{2-} could be neglected around the pH about 4.7. By rearranging equation (2), the following relation can be obtained.

$$\begin{aligned} \log \frac{[MHI^-]}{[H_3I^-]'} &= \log K_{MHI} \cdot k_2 \cdot k_3 + \log [M^{2+}] \\ &\quad - 2 \log [H^+]^{\alpha_{H(H_3I)}} \frac{1}{2} \quad (3) \end{aligned}$$

When the concentration of metal ion added is about 100 fold excess with that of ALC added, as $[M^{2+}]$ value may be safely assumed to be C_M , equation (3) indicates that a plot of $\log [MHI^-]/[H_3I^-]'$ against $\log [H^+]^{\alpha_{H(H_3I)}} \frac{1}{2}$ may give a straight line with a slope of two units, and K_{MHI} can be calculated from the point where a $\log [MHI^-]/[H_3I^-]'$ is equal to zero.

The stability constant, maximum of the absorption spectrum of these metal complex and a slope of equation (3) are listed in Table 3. The linear relation has been observed between the value of $\log [MHI^-]/[H_3I^-]'$ and $\log [H^+]^{\alpha_{H(H_3I)}} \frac{1}{2}$ with a slope of two units. Therefore, this relation can be confirmed that the complex formation reaction with ALC follows the equilibrium of equation (1).

Table 3. Stability Constant

Metal Ion	$\log K_{MHI}$	λ_{max}	Slope of eq. (3)
Cu	11.76	506	-1.98
Cd	10.20	508	-1.96
Zn	11.94	484	-2.04
Ni	12.98	506	-2.00
Co	12.08	500	-2.08
Pb	13.23	486	-2.05

Polarographic Behaviors of Organic Reagents

D.c. and a.c. polarograms of ALC and PC in sodium acetate buffer solution (pH 6.0), thio-oxine in Britton-Robinson buffer solution (pH 2.0) and MTB in boric acid-sodium hydroxide buffer solution (pH 10.0) are illustrated in Fig. 3 and Fig. 4, respectively. D.c. and

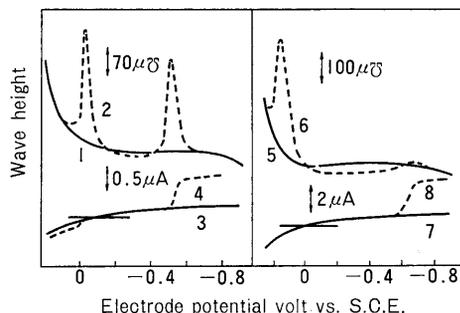


Fig. 3. D.c. and a.c. polarographic waves of ALC and PC in 0.2M NaOAc buffer solution of pH 6.0. (1) : a.c. base current, (2) : (1)+ $10^{-5}M$ ALC, (3) : d.c. base current, (4) : (3)+ $2 \times 10^{-4}M$ ALC, (5) : a.c. base current, (6) : (5)+ $2 \times 10^{-5}M$ PC, (7) : d.c. base current, (8) : (7)+ $10^{-3}M$ PC.

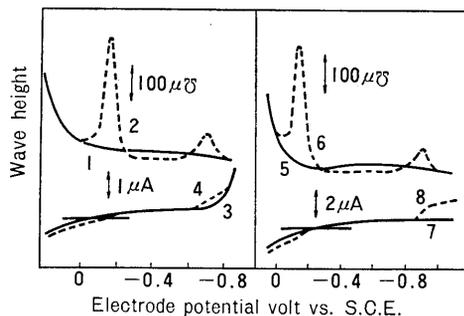


Fig. 4. D.c. and a.c. polarographic waves of thio-oxine and MTB. (1) : a.c. base current in Britton-Robinson buffer solution (pH 2.0), (2) : (1)+ $4 \times 10^{-5}M$ thio-oxine, (3) : d.c. base current, (4) : (3)+ $10^{-3}M$ thio-oxine, (5) : a.c. base current in sodium borate buffer solution (pH 10.0), (6) : (5)+ $2 \times 10^{-5}M$ MTB, (7) : d.c. base current, (8) : (7)+ $10^{-3}M$ MTB.

a.c. wave height, half wave potential and a.c. peak potential of these organic indicators are tabulated in Table 4.

D.c. wave height of ALC and phthalein complexone derivatives are exactly propor-

Table 4. D. c. and A. c. Polarographic Behaviors of Various Organic Reagents

Indicators	Measuring Conditions	D. c. id, $E_{1/2}V.$		A. c. ip, Ep V.	
		$\mu A.$	vs. S. C. E.	μC	vs. S. C. E.
oxine	$4 \times 10^{-5}M$, pH 6.5*	—	—	512	-0.05
		****	-1.0	—	—
5-fluoro-oxine	$4 \times 10^{-5}M$, pH 7.0*	—	—	412	-0.06
		0.14	-1.22	—	—
thio-oxine	$4 \times 10^{-5}M$, pH 2.0*	—	—	467	-0.21
		****	-0.7	66	-0.73
ALC	$10^{-5}M$, pH 6.0**	—	—	480	+0.06
		0.10	-0.48	305	-0.47
TPC	$2 \times 10^{-5}M$, pH 6.0**	—	—	580	-0.04
		0.11	-0.85	105	-0.86
PC	$2 \times 10^{-5}M$, pH 6.0**	—	—	420	+0.21
		0.09	-0.63	20	-0.60
PPC	$2 \times 10^{-5}M$, pH 5.0**	—	—	380	+0.15
		0.08	-0.83	—	—
Calcein	$2 \times 10^{-5}M$, pH 5.0**	—	—	290	± 0.0
		0.07	-0.95	—	—
MTB	$2 \times 10^{-5}M$, pH 10.0***	—	—	370	-0.09
		0.03	-0.87	55	-0.90
XO	$2 \times 10^{-5}M$, pH 5.0**	—	—	140	-0.04
		0.02	-0.90	—	—

* Britton-Robinson buffer solution

**** indistinct wave

** 0.2M NaOAc-HOAc buffer solution

*** 0.2M NaOAc- $Na_2B_4O_7$ buffer solution

tional to the square root of the effective mercury pressure and to the bulk concentration of these indicators. This clearly indicates that these reduction wave have the properties of diffusion control. D. c. wave of oxine and thio-oxine cannot be measured exactly as these d. c. polarograms have an indistinct shape. ALC gives a reversible two electron reduction wave in acetate buffer solution of pH 6.0 at $-0.48V$ vs. S. C. E., which corresponds to the reduction of carbonyl bond of anthraquinone.¹⁵⁾ Within the pH range from 2 to 11, the relation between a pH value and the half wave potential of ALC gives a straight line with the slope of 62mV. (Fig. 5) As is shown by the equation (4), this fact shows that the reduction step of ALC seems to involves two hydrogen ions and two

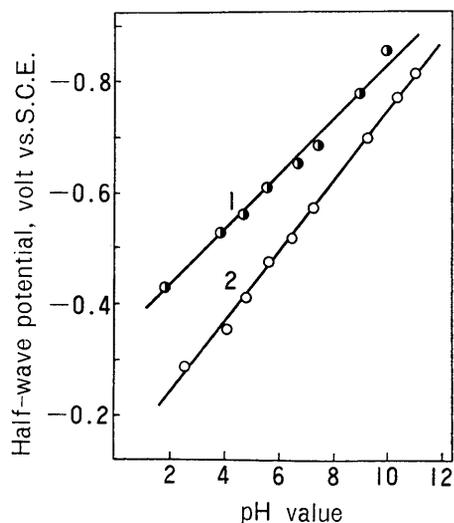


Fig. 5. Effect of pH on the half-wave potential of ALC and PC. 1: Concentration of PC, $10^{-3}M$; 2: Concentration of ALC, $2 \times 10^{-4}M$, Buffer system: HOAc- H_3BO_3 -NaOH

ALC was estimated to be $6 \times 10^{-5} M$ at $25^\circ C$ from the preliminary experiment of conductivity measurement.¹⁹⁾

The dependence of the first a.c. wave height of these indicators on the dropping rate of mercury was studied. The result of PC is shown in Fig. 7. Evidently, a.c. wave

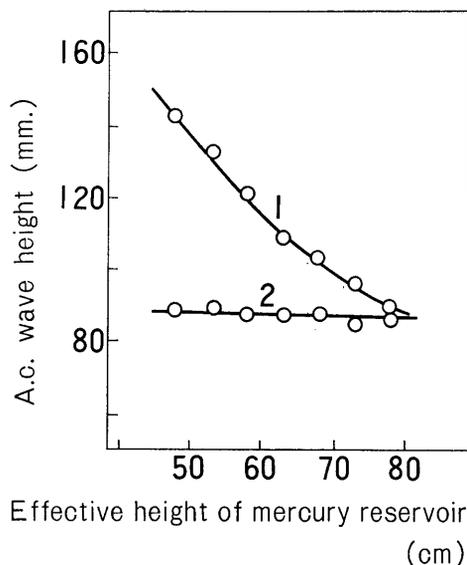


Fig. 7. Effect of height of mercury reservoir on the a.c. wave height of PC.

1: Concentration of PC, $2 \times 10^{-5} M$, recorder sens. $4.0 \mu\bar{V}/mm$.

2: Concentration of PC, $5 \times 10^{-4} M$, recorder sens. $20.0 \mu\bar{V}/mm$.

Buffer system: NaOAc-HOAc, pH 6.0.

height does not change with head of mercury column beyond a concentration of PC at which adsorption reaches a limiting value. On this basis, it is concluded that the first a.c. wave of these indicators has a tensammetric nature.

Effect of pH on the Tensammetric Wave Height: Behaviors of the tensammetric wave of these indicators change remarkably with the variation of pH, because the dissociable hydroxyl group or acetic acid group are involved in the molecule or ion. Fig. 8 to Fig. 11 illustrate the effect of pH on the tensammetric wave height of these indicators.

Oxine derivatives exist as H_2I^+ , HI and I^- in aqueous solution, and these ratio changes with the pH value. Under the pH range in which the maximum tensammetric wave height

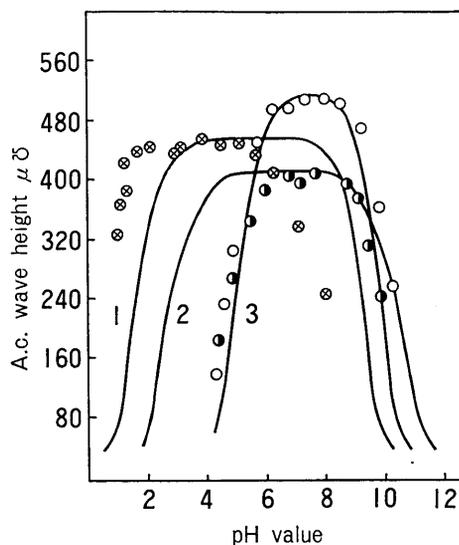


Fig. 8. Effect of pH on the tensammetric wave height of oxine derivatives. Concentration of oxine derivatives: $4 \times 10^{-5} M$, Britton-Robinson buffer solution.

Distribution of HI species, 1: thio-oxine, 2: 5-fluoro-oxine, 3: oxine,

Experimental plots of first a.c. wave height, ⊗: thio-oxine, ●: 5-fluoro-oxine, ○: oxine.

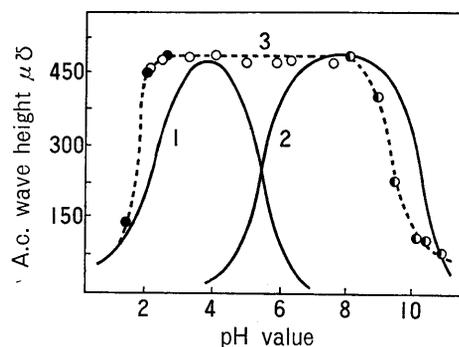


Fig. 9. Effect of pH on the tensammetric wave height of ALC.

1, 2: Distribution of ALC species, 1: H_3I^+ , 2: $H_2I_2^{2-}$, 3: Experimental results of the first a.c. wave height at the concentration of $10^{-5} M$ ALC.

●: HNO_3 - KNO_3 buffer solution,

○: HOAc-NaOAc buffer solution

⊙: NH_4OAc - NH_3 buffer solution.

occurs, oxines chiefly correspond to the neutral species, HI .¹⁸⁾ Thio-oxine is very easily oxidized to the disulfide in neutral or alkaline solution even with the addition of hypophosphorous acid in the electrolyte solution.¹¹⁾ Therefore, the region in which

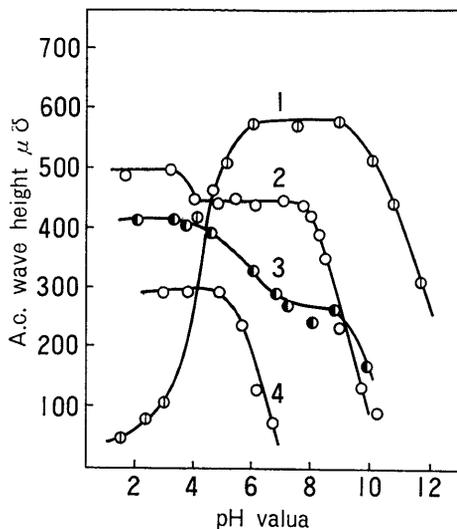


Fig 10. Effect of pH on the tensammetric wave height of phthalein complexone derivatives.

Concentration of phthalein complexone derivatives: $2 \times 10^{-5} M$, Buffer system: HOAc-boric acid-NaOH solution ($\mu=0.2$)
1: TPC, 2: PC, 3: PPC, 4: calcein.

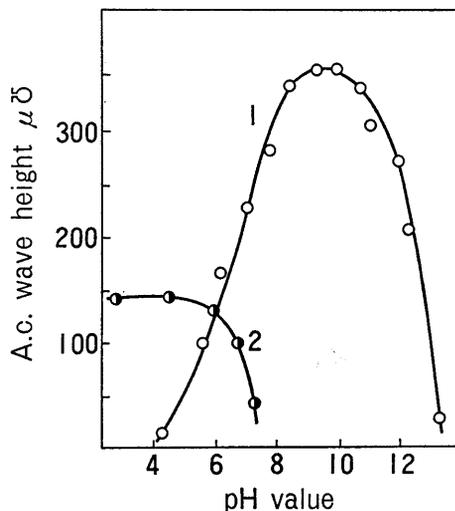


Fig 11. Effect of pH on the tensammetric wave height of sulfophthalein complexone derivatives.

Concentration of sulfophthalein complexone derivatives: $2 \times 10^{-5} M$, Buffer system: HOAc-boric acid-NaOH solution ($\mu=0.2$)
1: MTB, 2: XO.

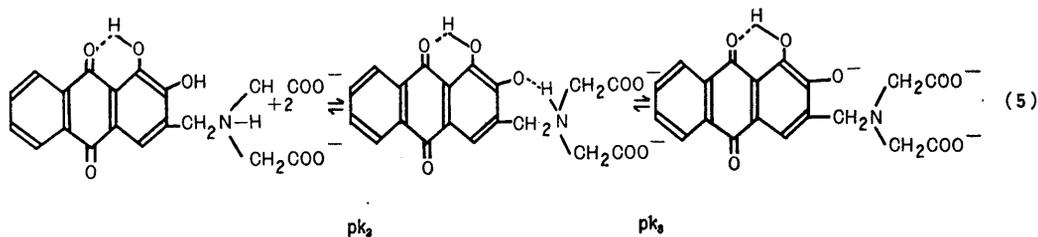
the constant a.c. wave height occurs does not agree with measurement.

As is obvious from the results in Fig 9, the adsorption wave of ALC is observed in the pH range in which the dominant species are H_3I^- and H_2I^{2-} . ALC has four ionisable protons and the dissociation equilibria are expressed in equation (5).¹⁰⁾ Around the pH in which the third stage dissociation of ALC occurs, hydrogen bonding between the 2-hydroxyl group and ammonium hydrogen is broken and anthraquinone ring shows an ionic nature. This may be closely related to disappearance of the adsorption wave.

The adsorption wave height of ALC is much greater than that of oxine, because the adsorption of aromatic compounds on a

positively charged mercury surface increases with an increase in the number of conjugated double bonds of adsorbates.²⁰⁾ The same behaviors as above considerations were also observed in the case of the adsorption of pyridine, quinoline and acridine.²¹⁾

In the case of phthalein complexone derivatives, dependence of a.c. wave upon the pH range in which adsorption reaches a limiting value showed the same behaviors as that of ALC. Since phthalein complexone derivatives involves four acetic acid groups and two hydroxyl groups, the adsorption cease to take place as a result of formation of HI^{5-} beyond the pH value equal to pk_5 . It is to be expected from the acid dissociation constant that the pH range in which the



maximum tensammetric wave appears is spreaded over the more alkaline region in the order of calcein < PPC < PC < TPC. The experimental results were in agreement with expected order. On the other hand, adsorption wave height of phthalein complexone derivatives at the concentration of $2 \times 10^{-5} M$ also increase in the same order. PC is more surface active than PPC. This behavior may be explained by assuming that π -orbital interaction forces with benzen rings increase as methyl group is introduced, because the positive side of dipole of methyl substitution product arises on these methyl groups. Adsorption wave height of sulfophthalein complexones are too small to be compared with that of phthalein complexones. Since an anionic indicator is less easily adsorbed with increasing negative charge, the adsorption of the sulfonic acid group decreases comparing with that of carboxyl group in aqueous solution. Fig. 12 shows the effect of pH on the tensammetric peak potential of oxine, ALC, phthalein complexones and sul-

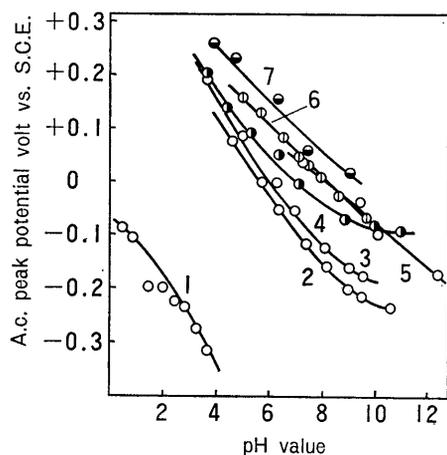


Fig. 12. Effect of pH on the tensammetric peak potential of various indicators. Indicator concentration: oxine derivatives, $4 \times 10^{-5} M$; ALC, $10^{-5} M$, phthalein complexones and sulfophthalein complexones: $2 \times 10^{-5} M$. Buffer system: Britton-Robinson buffer for oxines and NaOH-HOAc-boric acid buffer for the others. 1: thio-oxine, 2: oxine, 3: 5-fluoro-oxine, 4: ALC, 5: MTB, 6: PPC, 7: PC.

fophthalin complexones. Peak potential of these waves are generally observed at more positive potential than the electrocapillary maximum (e.c.m.) and are shifted to more negative potential as a pH value increases.

Dependence of the Tensammetric Wave Height upon the Concentration of Indicators: When van der Waals interaction forces among the adsorbed molecules or ions can be ignored, the Langmuir adsorption equation is established.

$$\theta = BC / (1 + BC) \quad (6)$$

where B and C represent the Langmuir adsorption coefficient and the surfactant concentration. The fraction of the surface coverage $\theta = \Gamma / \Gamma_m$, Γ is the surface excess and Γ_m is the limiting value of Γ at $C \rightarrow \infty$. The peak height of the tensammetric wave, Δi_s , is proportional to the surface coverage θ , and the following equation can be expressed as k for its proportionality factor.²²⁾

$$\Delta i_s = kBC / (1 + BC) \quad (7)$$

Fig. 13 and Fig. 14 show the relation between the tensammetric wave height and the corresponding concentration of indicators such as oxines in Britton-Robinson buffer solution and ALC, TPC, PC and PPC in sodium acetate buffer solution. Except for the case

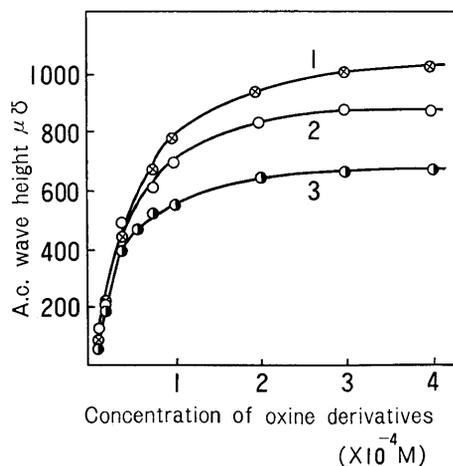


Fig. 13. Dependence of the tensammetric wave height upon the concentration of oxine derivatives. Britton-Robinson buffer solution. 1: thio-oxine, pH 2.0 2: oxine, pH 6.5; 3: 5-fluoro-oxine, pH 8.5.

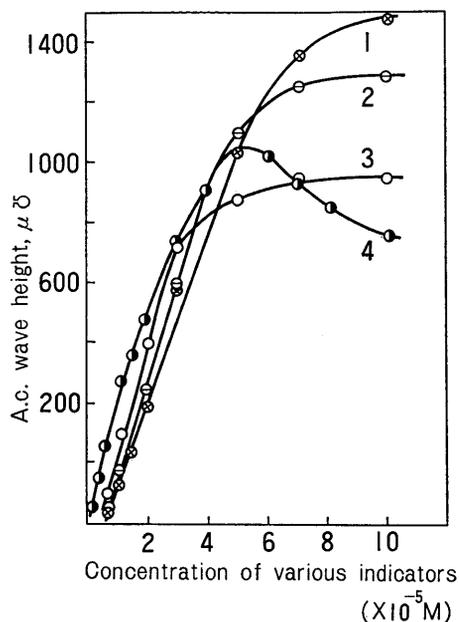


Fig. 14. Dependence of the tensammetric wave height upon the concentration of various indicators.

NaOAc-HOAc buffer solution, 1: PPC, pH 5.0; 2: PC, pH 6.0; 3: TPC, pH 6.0; 4: ALC, pH 6.0.

of ALC, the shape of the curves were found to follow a typical Langmuir type relation. By means of the equation (7) the value of TPC at pH 6.2, PC at pH 6.0 and PPC at pH 5.0 are determined to be 2600, 1770 and 1300 μV for k and 1.85×10^4 , 5.29×10^4 and 8.28×10^4 1/mol for B , respectively. In the concentration range in which the adsorption reaches the saturation and the wave height reaches a limiting value, the wave height increases in the order of $\text{TPC} < \text{PC} < \text{PPC}$. (curves 1~3 in Fig. 14) In contrast to the above relation, however, in the concentration range in which the wave height is proportional to the bulk concentration of these indicators, the wave height increases conversely in the order of $\text{PPC} < \text{PC} < \text{TPC}$. This phenomenon may be understood as the following explanation. In the concentration range in which the wave height is proportional to the bulk concentration of indicator, the adsorbability increases in the order of $\text{PPC} < \text{PC} < \text{TPC}$. However, beyond the concentration at which the wave

height reaches a limiting value, the concentration of adsorbed species decreases with an increase in the area occupied by these single molecule on the mercury surface.

The tensammetric wave height of ALC increases with the concentration up to 5×10^{-5} M, while its wave height decreases with the concentration above 6×10^{-5} M. This result deviates from a Langmuir type relation. The reason of this peculiar phenomenon cannot be explained clearly, however, as has been found in the case of the measurements of a temperature coefficient, it may be considered that the decrease of this wave is due to the association of ALC in the solution. Fig. 15 illustrates the dependence of the tensammetric peak potential upon the concentration of various indicators. There are little change with the difference of the indicator concentration.

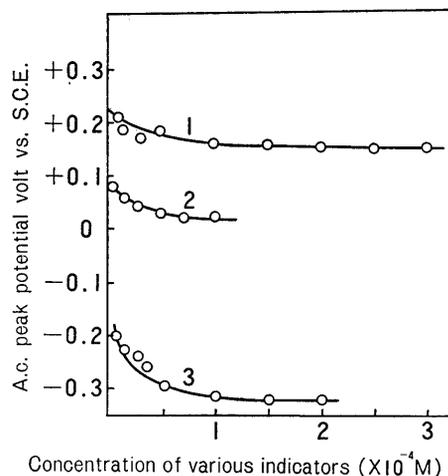


Fig. 15. Dependence of the tensammetric peak potential upon the concentration of various indicators.

1: PC, HOAc-NaOAc buffer solution, pH 6.0, 2: ALC, HOAc-NaOAc buffer solution, pH 6.5 3: thio-oxine, Britton-Robinson buffer solution, pH 2.0,

Electrocapillary Curves: Adsorption of the surface active molecule or ion on the mercury drop surface lowers the interfacial tension at the mercury-solution interface and changes the electrocapillary curve. At a constant rate

of flow of mercury, the drop time (t) is proportional to the interfacial tension (γ); $\gamma = \delta t$.²³⁾ The value of δ is a constant for the capillary. The proportionality factor (δ) for the capillary used in this experiment was determined to be $86.1 \text{ erg}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ from the drop time of the known interfacial tension at the e.c.m. in the solution of water-ethanol mixture.²⁴⁾ Thereby, drop time potential curves usually measured in polarography can be easily converted to interfacial tension versus potential curves. Electrocapillary curves of various indicators, such as thio-oxine, ALC, PC and TPC, are shown in Fig. 16-A.B.C.D., respectively. Thio-oxine lowers the interfacial tension and adsorbs over the whole potential range. The adsorption on the

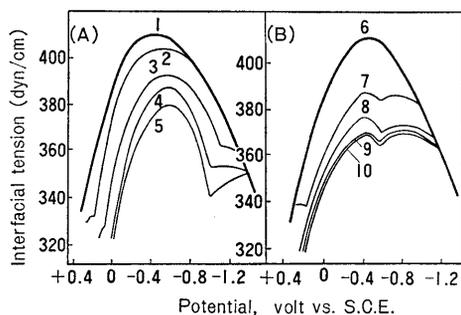
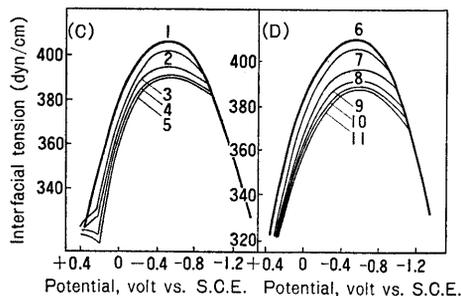


Fig. 16. Electrocapillary curves.

- (A): Thio-oxine concentration, 1: 0; 2: $4 \times 10^{-5} M$; 3: $10^{-4} M$; 4: $2 \times 10^{-4} M$; 5: $10^{-3} M$, (B.R. buffer pH 2.0)
 (B): ALC concentration, 6: 0; 7: $5 \times 10^{-5} M$; 8: $10^{-4} M$; 9: $5 \times 10^{-4} M$; 10: $10^{-3} M$, (acetate buffer pH 6.0)



- (C): PC concentration, 1: 0; 2: $10^{-4} M$; 3: $5 \times 10^{-4} M$; 4: $10^{-3} M$; 5: $2 \times 10^{-3} M$, (acetate buffer pH 6.0)
 (D): TPC concentration, 6: 0; 7: $10^{-4} M$; 8: $2 \times 10^{-4} M$; 9: $5 \times 10^{-4} M$; 10: $10^{-3} M$; 11: $2 \times 10^{-3} M$, (sodium borate buffer pH 10.0)

negative side of e.c.m. is mainly caused by the coulombic interaction,²⁵⁾ because the nearly half of thio-oxine exists as H_2I^+ at pH 1.9. Except for the case of thio-oxine, these indicators mainly lower the interfacial tension at potentials more positive than the e.c.m. The abnormal depression was observed in the electrocapillary curves of ALC at the potential about $-0.5V$. This depression corresponds roughly with the potential where the d.c. reduction wave appears.

The relation between the interfacial tension and the surface excess of the adsorbates at the mercury-solution interface can be expressed by the Gibb's adsorption equation (8).

$$d\gamma = -\sum_i \Gamma_i d\mu_i = -RT \sum_i \Gamma_i d(\ln C_i) \quad (8)$$

where Γ_i , μ_i and C_i represent the surface excess per cm^2 , the chemical potential and the concentration of the i -th component of the solution, respectively. Since the present experiment can be provided that the total concentration of the adsorbable species corresponds to C , the surface excess can be calculated by measuring the value of $d\gamma/d(\ln C)$ at the fixed potential and constant ionic strength. Fig. 17-A.B.C.D. and Fig. 18-A.B.C.D. show the variation of the surface excess with the electrode potential and with the concentration of indicators, respectively.

If the saturated surface excess (Γ_m) of

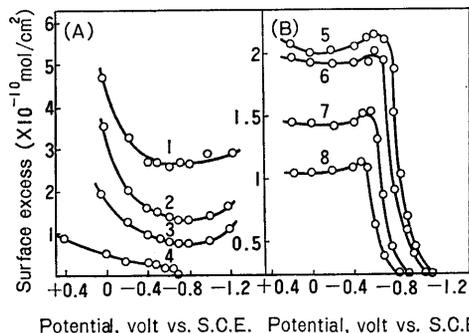
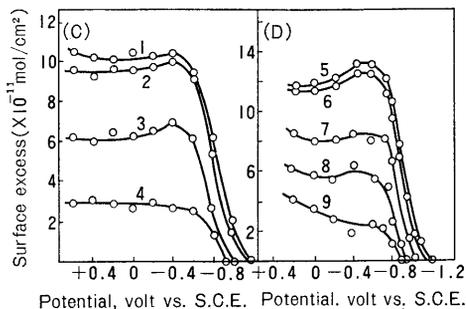


Fig. 17. Variation of surface excess with electrode potentials.

- (A): Thio-oxine concentration, 1: $10^{-3} M$; 2: $2 \times 10^{-4} M$; 3: $10^{-4} M$; 4: $4 \times 10^{-5} M$, (B.R. buffer pH 2.0)
 (B): ALC concentration, 5: $10^{-3} M$; 6: $5 \times 10^{-4} M$; 7: $10^{-4} M$; 8: $5 \times 10^{-5} M$, (acetate buffer pH 6.0)



(C): PC concentration, 1: $2 \times 10^{-8} M$; 2: $10^{-8} M$; 3: $5 \times 10^{-4} M$; 4: $10^{-4} M$, (acetate buffer pH 6.0)
 (D): TPC concentration, 5: $2 \times 10^{-8} M$; 6: $10^{-8} M$; 7: $5 \times 10^{-4} M$; 8: $2 \times 10^{-4} M$; 9: $10^{-4} M$, (sodium borate buffer pH 10.0)

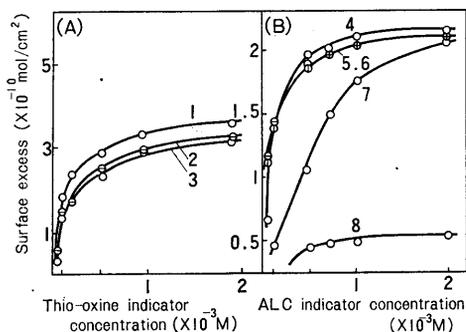
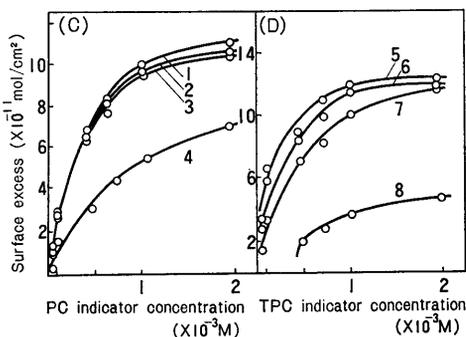


Fig. 18. Variation of surface excess with the concentration of indicator.
 (A): Thio-oxine, Electrode potential 1: $-0.4 V$, 2: $-0.8V$, 3: $-1.2V$ vs. S.C.E.
 (B): ALC, Electrode potential 4: $-0.6V$, 5: $-0.4V$, 6: $0V$, 7: $-0.8V$, 8: $-1.0V$ vs. S.C.E.



(C): PC, Electrode potential 1: $-0.4V$, 2: $0V$, 3: $+0.4V$, 4: $-0.8V$ vs. S.C.E.
 (D): TPC, Electrode potential 5: $-0.4V$, 6: $0V$, 7: $-0.8V$, 8: $-1.0V$ vs. S.C.E.

thio-oxine, ALC, PC and TPC for the monolayer adsorption is assumed to be 3.2×10^{-10} , 2.1×10^{-10} , 10.8×10^{-11} and 1.2×10^{-10} mol/cm², the area occupied by these single molecule

can be calculated as 52 \AA^2 , 79 \AA^2 , 154 \AA^2 and 138 \AA^2 , respectively. The area of the electrode occupied by a molecule of quinoline,²⁵⁾ which is considered to be smaller than that of oxine derivatives, has been reported to be 60 \AA^2 when it is adsorbed to form a monolayer in parallel to the electrode surface, and that of methylene blue²⁶⁾ has been reported to be 100 \AA^2 . These results are supported that the indicators studied here are adsorbed to form a stable monolayer in parallel to the electrode surface.

The theoretical consideration as stated above is only a rough approximation and is not enough to explain the relationship between the structure of the organic reagents on the mercury surface and its tensammetric wave. The above consideration, however, is a useful help in the understanding of some of the adsorption phenomenon and is useful to consider the possibility of a tensammetric wave as an end-point indicator of the complexometric titration of various metal cations.

Complexometric Titration using a Tensammetric Wave as an End-Point Indication

Tensammetric wave is very sensitive to the surfactant concentration as compared with the common a.c. polarographic wave. Tensammetric wave of the organic indicator utilized here disappears by the chelate formation with metals and reappears by the liberation of the indicator with the exchange reaction between the metal-indicator complex and a titrant such as EDTA. Therefore, when a small amount of the indicator is added before the titration, sharp S shape titration curve can be obtained and end-point of the metal ion can be detected by remarkable increase of the tensammetric wave caused by the liberation of the indicator near the equivalence point of metal. From the analytical view-points, the optimum titration conditions of metal ion depends on both the conditional stability constants of metal chelate and the characteristics of the indicator.

Laitinen and Sympson²⁷⁾ reported the complexometric titration method of calcium with the amperometric end-point detection using zincate ion as an indicator in sodium hydroxide solution. Since the conditional stability constant of EDTA chelate with zinc and calcium is satisfied with the relation of $K_{Ca'Y} > K_{Zn'Y}$, d.c. polarographic wave height of zincate ion decreases over the equivalence point of calcium. In order to obtain a sharp inflection point for the titration of calcium, the concentration of zincate ion must be maintained as small as possible. However, since the wave height with the concentration less than $10^{-4}M$ zincate ion cannot be determined accurately by d.c. polarographic method, titration of calcium in the concentration less than $10^{-4}M$ is inaccurate. Contrastively, when the tensammetric indicator is applied as an end-point detection in complexometric titration, a.c. wave height of indicator even with the concentration of the order of $5 \times 10^{-7}M$ can be satisfactorily determined, and the titrimetry with the proposed method in this paper could be carried out sensitively even in the metal concentration about $10^{-5}M$ with 0.001M EDTA.

Some optimum conditions for titration, such as the pH range in which the tensammetric wave reaches a limiting value, indicator concentration, ratio of the complex formation with metals and tensammetric wave height at the concentration of $10^{-5}M$, are

Table 5. Optimum Conditions of Indicators

Indicators	pH range	Optimum indicator concn. (mol/l)	Wave height (μV)	Molar ratio Metal/Ligand
oxine	5.5~8.5	10^{-5}	90	1:1, 1:2
5-fluoro-oxine	6~9	10^{-5}	60	1:1, 1:2
thio-oxine	1.5~4	10^{-5}	80	1:1, 1:2
ALC	2~8.5	2×10^{-6}	480	1:1
TPC	5~10	2×10^{-6}	280	2:1, 1:1
PC	2~8.5	5×10^{-6}	150	2:1, 1:1
PPC	1.5~7	5×10^{-6}	130	2:1, 1:1
MTB	8.5~11	5×10^{-6}	150	2:1, 1:1

shown in Table 5.

The usefulness of oxines for the end-point indicator are much less than the other indicators, because the wave height of oxines are relatively small and the mole ratio of complex formation shows 1-to-2 composition with metals. As is evident from Table 5, ALC is the most suitable indicator for the titration of metals in acidic and neutral solution and TPC is the most suitable indicator for that in neutral and alkaline solution.

Theoretical Titration Curve: when a metal M is titrated with a complexane Y using an organic reagent I as a tensammetric indicator, assuming the variation of pH during the titration can be ignored, the stoichiometric relationships of the total concentration of C_M , C_Y and C_I can be expressed, respectively.

$$C_M = [MY] + [MI]' + [M]' \quad (9)$$

$$C_Y = [MY] + [Y]' \quad (10)$$

$$C_I = [MI]' + [I]' \quad (11)$$

where $[M]' = [M]\alpha_{(M)}$ and $[Y]' = [Y]\alpha_{H(Y)}$, α is the side reaction coefficient of M and Y, respectively. $[I]'$ represents the total concentration of free indicator. $[MI]'$ is the total concentration of indicator which forms complex with metals. Equation (11) can be written as follows:

$$\begin{aligned} C_I &= [I]' + [MI] + 2[MI_2] + \dots \\ &= [I]' + [M]'[I]'(K_{M'I}' \\ &\quad + 2 \cdot K_{M'I}'K_{M'I'_2}[I]' + \dots) \quad (12) \end{aligned}$$

On solving the above equation for $[M]'$, the following relation can be obtained.

$$[M]' = \frac{C_I - [I]'}{[I]'} \cdot \frac{1}{(K_{M'I}' + 2 \cdot K_{M'I}'K_{M'I'_2} \cdot [I]' + \dots)} \quad (13)$$

Oxine and its derivatives may be expected to form complexes of 1-to-1 and 1-to-2 compositions with metals, and the other indicators form only a 1-to-1 chelate with metals. If the condition of $1 \gg 2 \cdot C_I \cdot K_{M'I'_2}$ is satisfied, the relation of $K_{M'I}' \gg 2 \cdot K_{M'I}'K_{M'I'_2} \cdot [I]'$ holds. Therefore, the value of $[M]'$ is sufficient to consider only the term of $K_{M'I}'$. On the other hand, when the relation of $K_{M'I}' \leq 2 \cdot K_{M'I}'K_{M'I'_2} \cdot [I]'$ occurs, the term of MI_2 must be considered. Combining the equation

(9), (10) and (11), C_Y is given as :

$$C_Y = C_M - (C_I - [I]') - [M]' + [Y]' \quad (14)$$

From the consideration of the conditional stability constant of MY, equation (15) can be obtained.

$$[Y]' = \{C_M - (C_I - [I]') - [M]'\} / [M]' K_{M'Y'} \quad (15)$$

Combining the above equation (13), (14) and (15) and designating C_Y/C_M as "a", the fraction "a" for the titration of M by Y is given by the expression.²⁸⁾

$$a = \frac{C_Y}{C_M} = 1 - \frac{C_I - [I]'}{[I]'} \cdot \frac{1}{C_M \cdot K_{M'Y'}} + \frac{[I]'}{C_I - [I]'} \cdot \frac{K_{M'I'}}{K_{M'Y'}} - \frac{1}{C_M} \left\{ \frac{[I]'}{K_{M'Y'}} + C_I - [I]' \right\} - \frac{1}{C_M K_{M'Y'}} \quad (16)$$

Under such conditions required for titration as $C_M > C_I$ and $K_{M'Y'} > K_{M'I'}$ hold, the value of $[I]' K_{M'I'} / C_M \cdot K_{M'Y'}$ and $1 / C_M \cdot K_{M'Y'}$ is much smaller than unity. Thus:

$$a = 1 - \frac{C_I - [I]'}{[I]'} \cdot \frac{1}{C_M \cdot K_{M'Y'}} + \frac{[I]'}{C_I - [I]'} \cdot \frac{K_{M'I'}}{K_{M'Y'}} - \frac{1}{C_M} (C_I - [I]') \quad (17)$$

This expresses the change in $[I]'$ during the titration. In equation (17) the second term on the right side is mainly concerned with the change in $[I]'$ before the equivalence point, and the third term is mainly concerned with that after the equivalence point. Moreover, as $C_I - [I]'$ may be assumed to be C_I before the equivalence point, the last term on the right side can be considered to be C_I/C_M , showing that the concentration ratio of the indicator to the metal ion (C_I/C_M) has direct effect upon the variation of "a" before the equivalence point. The smaller the value of the concentration ratio of the indicator to the metal ion, the sharper inflection point can be expected. Since the sensitivity of the tensammetric wave of the indicator utilized here is extremely high, the indicator of a very small concentration can be satisfactorily used for the titration. Therefore, the correction term of indicator concentration in equation (17) can be ignored and the titration can be applied to the metal ions of small concentration.

Effect of Indicator Concentration and Titration Concentration on the Titration Curve of Zinc:

At the constant initial concentration of zinc of $2 \times 10^{-5} M$ in acetate buffer solution, the effect of ALC concentration on the titration curve was studied. Moreover, at the constant initial concentration of ALC ion of $2 \times 10^{-6} M$, the effect of the titrant concentration on the titration curve of zinc was also examined.

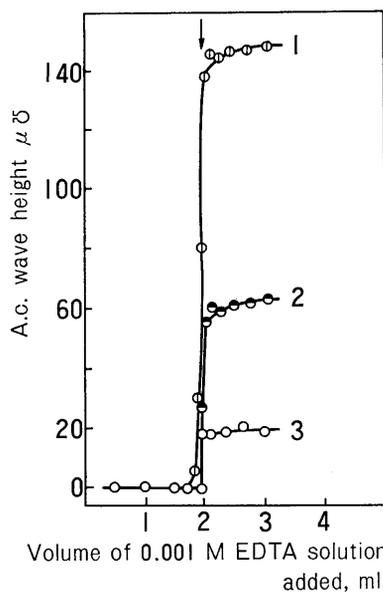


Fig. 19. Effect of ALC concentration on the titration curve of zinc.

Concentration of zinc: $2 \times 10^{-5} M$, NaOAc-HOAc buffer solution pH 6.0,

Concentration of ALC: 1: $5 \times 10^{-6} M$, 2: $2 \times 10^{-6} M$, 3: $10^{-6} M$.

Electrode potential: +0.05V vs. S.C.E.

Equivalence point was indicated by an arrow.

With increasing concentration of ALC, a small adsorption wave of indicator, which arises from the exchange reaction between metal-ALC complex and EDTA, is observed before the equivalence point of zinc ion and the sharp rising of the titration curve cannot be observed. (Fig. 19) In these titration conditions, as the value of $K_{M'I'} / K_{M'Y'}$ is sufficiently small, sharp inflection appears the point at which the indicator added is completely liberated. Therefore, the end-point

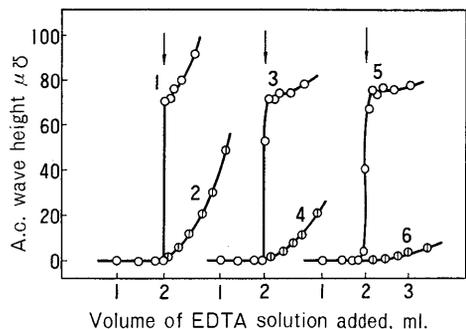


Fig. 20. Effect of titrant concentration on the titration curve of zinc.

Concentration of zinc; 1,2: $10^{-4}M$, 3,4: $4 \times 10^{-5}M$, 5,6: $2 \times 10^{-5}M$,

Concentration of ALC; 1,3,5: $2 \times 10^{-6}M$, 2, 4,6: 0, NaOAc-HOAc buffer solution, pH 6.0,

Concentration of titrant: 1,2: 0.005M, 3,4: 0.002M, 5,6: 0.001M,

Electrode potential: +0.05V vs. S.C.E., Equivalence point were indicated by arrows.

is located at the intersection of the tangent at the inflection point with the horizontal line of the a.c. wave.²⁹⁾

Optimum concentration of ALC was found to be $2 \times 10^{-6}M$ in this titration conditions. As is shown by the curve 5 in Fig. 20, the stability constant of zinc-ALC complex is sufficiently large, even if 0.001M EDTA is used as the titrant, satisfactory result is obtained.

In the titration with EDTA, the anodic wave is observed after the end-point of metal ion even in the absence of the tensammetric indicator. EDTA and its related chelating agent show a reversible anodic wave caused by the dissolution of mercury at the potential where the adsorption wave of indicator appears.³⁰⁾ Effect of pH on the a.c. polarographic wave height and peak potential of EDTA is shown in Fig. 21. Sensitivity of the anodic dissolution wave for EDTA is smaller than that of the a.c. wave of these tensammetric indicators. Therefore, when the titrant concentration less than 0.002M is used, end-point of metal ions is not disturbed by the presence of the excess titrant.

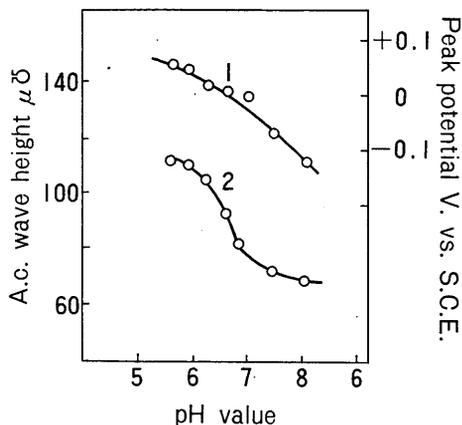


Fig. 21. Effect of pH on the a.c. wave height and peak potential of EDTA.

Concentration of EDTA: $4 \times 10^{-5}M$, NaOAc-HOAc buffer solution,

1: peak potential, 2: a.c. wave height.

Effect of pH on the Titration Curve of Metal Cations: As the stability constant of cadmium or manganese complex with these indicators is relatively small, titration curve of these cations is affected by the pH value. When the titration of $5 \times 10^{-5}M$ cadmium with 0.002 M EDTA using $5 \times 10^{-6}M$ oxine as a tensammetric indicator is carried out, the effect of pH on the titration curve is studied to be compared with the theoretical titration curves under the experimental conditions. (Fig. 22)

As is obvious from the equation (17), the change in $[I]'$ before the equivalence point is mainly concerned with the value of $1/C_M \cdot K_{M'} I'$. The smaller the value of $1/C_M \cdot K_{M'} I'$, the sharper end-point can be expected. Experimental values agreed well with the calculated titration curves. Below the pH about 7.5, the tensammetric wave of liberated oxine is observed before the end-point of cadmium, and the sharp rising of the titration curve cannot be observed. However, the conditional stability constant of cadmium-oxinate complex increases with an increase in the pH value, and the wave of liberated oxine before the equivalence point can be neglected at pH 8.0, and accurate end-point can be observed.

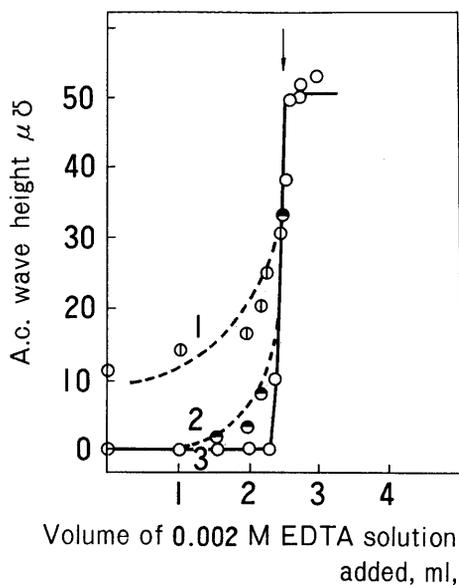


Fig. 22. Effect of pH on the titration curve of cadmium.

Concentration of cadmium: $5 \times 10^{-5} M$, Concentration of oxine: $5 \times 10^{-6} M$, Experimental value; \odot : pH 7.0, \bullet : pH 7.5, \circ : pH 8.0, Theoretical curve; 1: pH 7.0, 2: pH 7.5, 3: pH 8.0, Buffer system: $\text{NH}_4\text{OAc}-\text{NH}_3$ buffer solution, Electrode potential: $-0.05V$ vs. S.C.E., Equivalence point was indicated by an arrow.

Titration Curve of Various Metal Cations:

Complexometric titration of various metal cations with EDTA were carried out. Titration curves of lead and indium are shown in Fig. 23.

Recovery of various metal cations under the optimum titration conditions and titration error are presented in Table 6. Since the end-point is usually determined by a graphical method from the intersection point with the titration curve, the results obtained are expected a positive error in all cases.²⁹⁾ When calcium or manganese are titrated, the conditional stability constant of these metal-indicator complex is comparatively small, and some positive error was observed. However, since the tensammetric wave is very sensitive to the indicator concentration, various metal cations even in a concentration less than 0.4 mg/100ml can be satisfactorily

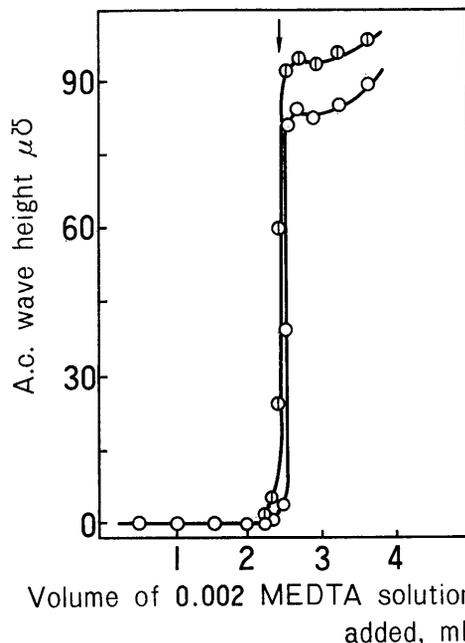


Fig. 23. Titration curve of indium and lead. Concentration of indium or lead: $5 \times 10^{-5} M$, Concentration of PC: $5 \times 10^{-6} M$, \odot : indium in $\text{HOAc}-\text{HClO}_4$ buffer solution, pH 3.0, \circ : lead in $\text{NaOAc}-\text{HOAc}$ buffer solution, pH 6.0, Electrode potential: $+0.2V$ vs. S.C.E. Equivalence point was indicated by an arrow.

titrated within 1.5% relative error by this method.

Apparatus and Reagents

Apparatus: All the polarograms were measured with a Yanagimoto PA-101 type pen recording polarograph. A dropping mercury electrode with the rate of the flow of mercury, m , of $1.746 \text{ mg} \cdot \text{sec}^{-1}$ and the drop time, t , of 4.75 sec at a mercury height of 69.5cm into an air-free 0.1M potassium chloride solution with open circuit was used. In a.c. polarographic measurements with an H type cell, a $200 \mu\text{F}$ condenser was connected in parallel to the cell to minimize the cell impedance. Electrocappillary curves were usually determined by the measurement of the drop time. All the absorption spectra were recorded with a Hitachi 124 type pen recording spectrophotometer using 50mm quartz cells.

Table 6. Recovery of Various Metal Cations under the Optimum Conditions.

Cations	Indicator concentration	pH value	Buffer system	Taken mg/100ml	Found mg/100ml	Error %
Cu	$5 \times 10^{-6}M$ oxine	6.0	NaoAc-HoAc	0.254	0.258**	+1.58
	$2 \times 10^{-6}M$ ALC	6.0	NaoAc-HoAc	0.127	0.129*	+1.57
Cd	$5 \times 10^{-6}M$ oxine	8.0	NH ₄ oAc-NH ₃	0.450	0.460**	+2.22
	$2 \times 10^{-6}M$ ALC****	6.0	NaoAc-HoAc	0.225	0.229*	+1.78
Zn	$2 \times 10^{-6}M$ ALC	6.0	NaoAc-HoAc	0.131	0.132*	+0.76
	$2 \times 10^{-6}M$ TPC	6.0	NaoAc-HoAc	0.131	0.130*	-0.76
Ni	$5 \times 10^{-6}M$ oxine	6.5	NaoAc-HoAc	0.234	0.238**	+1.70
	$2 \times 10^{-6}M$ ALC	6.0	NaoAc-HoAc	0.117	0.116*	-0.85
Co	$5 \times 10^{-6}M$ oxine	6.5	NaoAc-HoAc	0.236	0.240**	+1.70
	$2 \times 10^{-6}M$ ALC	6.0	NaoAc-HoAc	0.118	0.120*	+1.69
Mn	$5 \times 10^{-6}M$ oxine****	8.5	NaoAc-Na ₂ B ₄ O ₇ +Na tart.	0.442	0.456**	+3.16
	$2 \times 10^{-6}M$ ALC	6.5	NaoAc-HoAc	0.221	0.230*	+4.07
Pb	$2 \times 10^{-6}M$ ALC	6.0	NaoAc-HoAc	0.414	0.413*	-0.24
	$5 \times 10^{-6}M$ PC	6.0	NaoAc-HoAc	0.414	0.418**	+0.97
In	$5 \times 10^{-6}M$ oxine	6.0	NaoAc-HoAc+Na tart.	0.230	0.235**	+2.17
	$2 \times 10^{-6}M$ ALC	3.0	NaoAc-HClO ₄	0.230	0.232*	+0.87
Th	$2 \times 10^{-6}M$ ALC	3.0	NaoAc-HClO ₄	0.464	0.468*	+0.86
Bi	$2 \times 10^{-6}M$ ALC	3.0	NaoAc-HClO ₄	0.418	0.422*	+0.95
Ca	$5 \times 10^{-6}M$ TPC****	10.0	NaoAc-NaOH	0.320	0.331***	+3.43

* 0.001M EDTA was used as titrant.

** 0.002M EDTA was used as titrant.

*** 0.002M CyDTA was used as titrant.

**** Small a. c. wave of liberated indicator appeared before the end-point of metal.

Photometric titration curves were determined by using a Yanagimoto PG-2 type spectrophotometer with a photometric titration adapter. The determination of acid dissociation constant by the pH titration was carried out in an atmosphere of nitrogen.

Reagents: The reagent grade oxine was used without further purification. 5-fluoro-oxine was purified by vacuum sublimation at 80°C (mp. 110°C). Thio-oxine, Dotite reagent, was treated with hypophosphorous acid and was recrystallized by the procedure proposed by H. Freiser et. al.¹¹⁾ As thio-oxine is easily oxidized to the disulfide in contact with air, a stock solution of thio-oxine was prepared by mixing 1% hypophosphorous acid solution. Alizarin complexone, Dotite reagent, was recrystallized from acetic acid sodium acetate

solution (pH 4.3) by the procedure proposed by T. S. West et. al.³¹⁾ This purified compound is decomposed at 188°C. Phthalein complexone derivatives, Dotite reagent, were recrystallized from hydrochloric acid solution according to the method in the literature.¹²⁾ Since these reagents were not available in a pure state, the concentration of stock solution was determined by the photometric titration with the standard cadmium solution. A purity of these reagents was 84.94% for TPC, 91.89% for PC and 88.70% for PPC, respectively. The stock solution of phthalein complexone derivatives was prepared from sodium acetate solution. As they decompose rapidly with time, indicator solution was prepared afresh each day.

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