The Amperometric Titration of Metal(II) Ions with *trans*-1,2-Cyclohexanediamine-*N*,*N*,*N*′,*N*′-tetraacetate (CyDTA)

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(Received March 22, 1975)

The use of CyDTA in the amperometric determination of metal-ion mixtures was studied systematically. Because of the sluggishness of the nickel(II)-EDMA~CyDTA substitution reaction, the nickel(II) ion in the EDMA solution could be masked completely in respect to the CyDTA. Therefore, even in the presence of an excess of nickel(II)ions, the copper(II), lead(II), cobalt(II), cadmium(II), and zinc(II) ions in the EDMA solution at about pH=6.50 could be determined accurately with CyDTA. In the amperometric titration of binary mixture of copper(II) and zinc(II), lead(II), cadmium(II), or cobalt(II) ions in the EDMA solution, titration curves with two sharp breaks could be obtained by following the change in the diffusion current due to the reduction of the copper(II)-EDMA complex. The first and second breaks correspond, respectively, to the equivalence point of zinc(II), lead(II), cadmium(II), or cobalt(II) and to that of copper(II).

Chelatometric titrations play an increasingly important role in the analysis of metal-ion mixtures. To widen the scope of these applications, a great number of methods of selective titrations have been proposed. However, the selectivity in the chelatometric titration of a mixture of metal ions has very often been discussed only from the thermodynamic point of view,[1] and the reaction rate effect on the titration has been disregarded. Therefore, it seems worthwhile to discuss this phenomenon from both thermodynamic and kinetic points of view in predicting the optimum conditions necessary for selective titrations. In this paper, the amperometric titration of metal-ion mixtures in an EDMA solution will be studied by using CyDTA as a titrant and will be discussed from both thermodynamic and kinetic points of view.

Experimental

Reagents. The CyDTA and diethylenetriaminepentaacetate (DTPA) used in this study were recrystallized from their aqueous solutions as their acids. The preparation and purification of the acid form of ethylenediaminemonoacetate (EDMA) were described in a previous paper.[2] All the other chemicals used were of an analytical-reagent grade and were used without further purification.

Apparatus and Experimental Procedures. All the DC current-voltage curves were measured with a Yanagimoto pen-recording polarograph P-8 or with a manual polarograph similar to Kolthof and Lingane's. The characteristic features of the dropping mercury electrode used were described previously.[3] All the other apparatus and the experimental procedures were the same as those in that paper. In this study, no buffer reagent was used, because the sample solutions contained a large excess of uncomplexed EDMA and had a sufficient buffer capacity in its pH ranges ($5.80<$ pH<7.70 and $8.50<$pH<10.50).

Results and Discussion

Let us consider the amperometric titration of the complexed metal ion, M, existing in the forms of MX and MX_2, with the chelon Z. If the reaction is rapid enough so that the equilibrium with respect to the formation reaction of MZ is practically maintained at every stage of the titration, the successful determination of M with Z is possible only when the conditional formation constant of MZ, K'_{MZ}, defined as $K'_{MZ}=[MZ]/([MX]+[MX_2])\cdot[Z]_f=K_{MZ}/(\alpha_H)_Z\cdot(K'_1\cdot[X]_f+K'_1\cdot K'_2\cdot[X]_f^2)$, is larger than $1\times10^4/C$, where C means the total concentration of the metal ion; $[X]_f$, the concentration of the uncomplexed X; K'_i, the i-th conditional successive formation constant of the M–X complex, and $(\alpha_H)_Z$, the (α_H) value of Z $(=1+[H^+]/K_n+\cdots+[H^+]^n/K_n\cdots K_1)$. Here, the charges are omitted for the sake of simplicity. Table 1 lists the K'_{MZ} values calculated for the reaction of CyDTA with metal ions in a 20 mM EDMA solution using the related equilibrium constants previously reported.[4,5] The K'_{MZ} values given in Table 1 show that if the reactions of CyDTA with metal ions in the EDMA solution are sufficiently rapid, 1.0 mM copper(II), nickel(II), cobalt(II), zinc(II), lead(II), and cadmium(II) ions in the 20 mM EDMA solution of pH=6.00 can be titrated successfully with CyDTA. In all cases other than the cobalt(II) system, the equivalence point was determined by following the change in the diffusion current of the metal(II)–EDMA complex, because the negative shift in the reduction potential at DME due to the complexation with CyDTA is sufficient. In the case of the cobalt(II) system, the course of the titration was followed by measuring the change in the oxidation wave-height of the cobalt(II)–EDMA complex at the DME. Typical titration curves obtained for the copper(II) and lead(II) ions are reproduced in Fig. 1. All the metal ions other than nickel(II) ion could be titrated accurately with CyDTA. In the case of the nickel(II) system, no end point could

TABLE 1. $\log K_e'$ FOR VARIOUS METAL(II)-IONS
$\mu=0.30$, 25 °C, $[EDMA]_f=20.0$ mM
$\log K'_{MZ}$ $(=K_{MZ}/(\alpha_H)_Z(K_1'\cdot[X]_f+K_1'\cdot K_2'\cdot[X]_f^2))$

Metal(II) ion	pH	
	6.00	6.50
Cu(II)	7.15	6.24
Ni(II)	9.30	8.84
Co(II)	11.10	10.95
Zn(II)	11.00	10.97
Pb(II)	11.98	11.87
Cd(II)	10.23	10.09

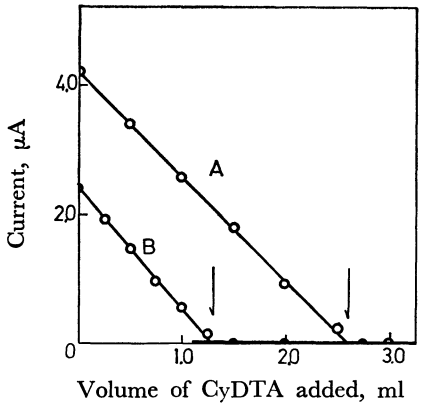

Fig. 1. Amperometric titration curves for the titration of 50 ml metal(II) solution with 19.2 mM CyDTA.
$[EDMA]_f=20.0$ mM, $\mu=0.30$, 25 °C
Equivalence points are indicated by arrows
A) 1.02 mM copper(II), B) 0.50_0 mM lead(II).

Table 2. Amperometric determination of metal(II) ions in the EDMA solution using CyDTA as a titrant

$\mu=0.30$, 25 °C, $[EDMA]_f=20.0$ mM
sample solution: 50 ml

Metal(II)	Metal(II) concn., mM	CyDTA concn., mM	Equivalence point, ml	
			Obsd	Calcd
Cu(II)	2.04	38.4	2.64	2.65
	1.02	19.2	2.65	2.65
	0.51_0	19.2	1.34	1.33
	0.20_4	3.84	2.68	2.65
Zn(II)	2.15	38.4	2.77	2.80
	1.07_5	19.2	2.79	2.80
	0.53_8	19.2	1.41	1.40
	0.21_5	3.84	2.82	2.80
Cd(II)	2.04	38.4	2.66	2.65
	1.02	19.2	2.64	2.65
	0.20_4	3.84	2.63	2.65
Pb(II)	2.00	38.4	2.62	2.60
	1.00	19.2	2.63	2.60
	0.20_0	3.84	2.57	2.60
Co(II)	1.82	38.4	2.38	2.38
	0.91_1	19.2	2.37	2.38
	0.18_2	3.84	2.40	2.38

be obtained. This can be ascribed to the slow reaction of CyDTA with the nickel(II)–EDMA complex in the EDMA solution. Some typical results are given in Table 2.

In the titration of a binary metal–ion mixture solution of M and M′ containing an excess of X and using Z as a titrant, when the equilibria with respect to the formation reactions of metal–Z complexes are always maintained, the optimum conditions for the selective titration can be easily predicted only from a theoretical consideration of the chemical equilibria involved. In this case, if the K'_{MZ} value for the M system is 1×10^4 times larger than that of the M′ system, M in the solution containing an equal amount of M′ will react preferentially with Z, hence, a titration curve with two sharp breaks, the first and second of which correspond to the equivalence points of M and M′ respectively, can be obtained by following the change in the concentration of M′. On the other hand, in cases where the reactions of Z with the metal complexes of X are rapid, while those of the metal–Z complexes formed during the course of the titration are very slow, the situation is complicated, because M, with a larger K'_{MZ} value, does not always react with Z at a rate larger than M′, which has a smaller K'_{MZ} value; hence, the formation of MZ may proceed not only through the direct reaction of the M–X complex with Z, but also through the exchange reaction of M′Z with the M–X complex. Therefore, if M′Z, with a smaller K'_{MZ} value, is substitution-inert, M can be titrated preferentially with Z only when the reaction of Z with M in the solution containing X proceeds much faster than that with M′. However, when the reaction of Z with M in the solution of X is much slower than that with M′, M′ will react first and can be titrated first with Z, irrespective of its smaller K'_{MZ} value. Thus, in the amperometric titration of the above binary mixture, when the course of titration is followed by determining the change in the limiting current of M′, the shape of the titration curve will depend on the relative rate constants of the reactions of Z with M and M′. The amperometric titration curves for such system can be calculated by using the following relation (1) for various reaction rates, assuming that the reaction of M′Z is completely substitution-inert:

$$r_{M'}=\frac{k_{M'}\cdot[M']_f}{k_{M'}\cdot[M']_f+k_M\cdot[M]_f}\times f_t \qquad (1)$$

where f_t is the total fraction titrated $(=C_Z/(C_M+C_{M'}))$; $r_{M'}$, the fraction of M′ reacted with Z; k_M and $k_{M'}$, the relative apparent rate constants, and $[M]_f$ and $[M']_f$, the metal-ion concentration at a given f_t value. The titration curves calculated for the equimolar mixture of M and M′ are reproduced in Fig. 2. The results shown in Fig. 2 clearly indicate that, if the rate constant ratio, $k_M/k_{M'}$, is smaller than 0.02, the

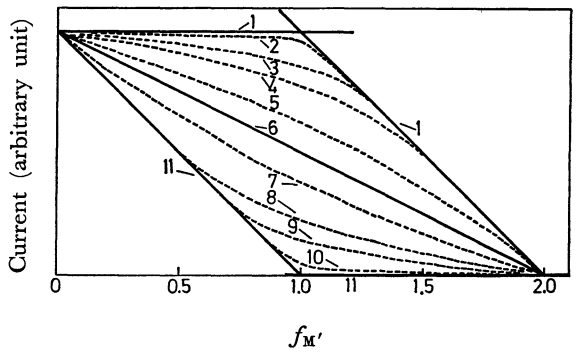

Fig. 2. Amperometric titration of an equimolar binary metal(II)-ion mixture of M and M′ with Z in the solution of X.
Titration curves were calculated at various rate constant ratio's, $R=k_M/k_{M'}$, under the conditions where $K'_{MZ}>K'_{M'Z}$, M′Z is substitution-inert, and the rate of the reaction of Z with M′–X complex is large sufficiently for the successful determination of M′.
$R=k_M/k_{M'}$ $f_{M'}=C_Z/C_{M'}$
1: >500, 2: 50, 3: 10, 4: 5, 5: 2, 6: 1, 7: 0.5, 8: 0.2, 9: 0.1, 10: 0.02, 11: <0.002.

titration curve shows only one break, corresponding to the equivalence point of M′, whereas if the $k_M/k_{M'}$ value is larger than 50, two break points occur, the former corresponding to the equivalence point of M, and the latter, to that of M′. Furthermore, if the $k_M/k_{M'}$ ratio is nearly identical to unity, the titration with Z will give only one break point, corresponding to the sum of M and M′.

The K'_{Mz} values in Table 1 show that all the EDMA complexes studied in this paper other than the copper(II) complex can replace the CyDTA anion thermodynamically from the copper(II)–CyDTA complex in the EDMA solution of pH=6.00 to 6.50. The kinetics of the reaction of the copper(II)–CyDTA complex with the EDMA complexes of zinc(II), lead(II), cadmium(II), cobalt(II), and nickel(II) ions in the EDMA solution was studied by observing the increase in the reduction wave-height of the copper(II)–EDMA complex in the pH range from 5.60 to 7.00. The reaction proceeds so slowly that the rate could not be determined accurately. However, the following results could be obtained in the preliminary experiments. In all the reactions studied except in the nickel(II) system, the rates 1) were independent of the concentrations of the zinc(II), lead(II), cadmium(II), and cobalt(II) ions and 2) were exactly proportional to the concentration of the copper(II)–CyDTA complex and that of the uncomplexed EDMA. Furthermore, 3) the plot of the product of the initial rate and $(\alpha_H)_{edma}/[H^+]$ against the hydrogen-ion concentration, $[H^+]$, gave a linear relation passing through the point of origin, provided that the other experimental conditions were kept constant (Fig. 3). In the nickel(II) system, no reduction step due to the copper(II)–EDMA complex could be observed. The above findings suggest the following reaction mechanism for the reaction of the copper(II)–CyDTA complex with the EDMA complexes of zinc(II), lead(II), cadmium(II), and cobalt(II) ions in the EDMA solution:

$$Cucydta^{2-} + H_2edma^+ \overset{k_{2H}}{\rightleftharpoons} Cu(edma)^+ + H_2cydta^{2-} \quad \text{rds} \qquad (2a)$$

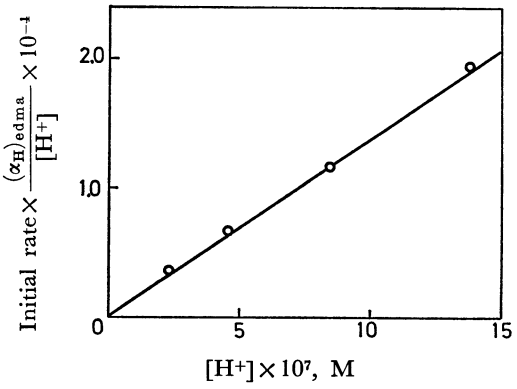

Fig. 3. The effect of the solution pH on the rate of the substitution reaction of copper(II)-CyDTA complex with zinc(II) ion in the EDMA solution.
μ=0.30, 25 °C, $[Cucydta^{2-}]$=1.0 mM
$[EDMA]_f$=30.0 mM, $[Zn(II)]_t$=10.0 mM
pH ranged from 5.80 to 6.80

$$M(edma)^+ + H_2cydta^{2-} \rightleftharpoons Mcydta^{2-} + H_2edma^+ \qquad (2b)$$
$$\downarrow\uparrow \quad \text{in a rapid equilibrium}$$
$$M(edma)_2^0$$

corresponding to the following relation:

$$\text{initial rate} = \frac{k_{2H}\cdot[Cucydta^{2-}]\cdot[edma]_f}{(\alpha_H)_{edma}\cdot K_3\cdot K_2} \times [H^+]^2 \qquad (3)$$

where K_i denotes the i-th deprotonation constant of H_3edma^{2+}. The k_{2H} value was determined to be $6.7\times10^{-3}\ M^{-1}\cdot s^{-1}$ from the slope of the above linear relation. The k_{2H} value thus determined suggests that only the 0.5% of the CyDTA anion coordinated to the copper(II) (1 mM) can be replaced by the 1 mM metal(II) ion in the 10 mM EDMA solution within an hour. As is clear from the above kinetic consideration of the titration of a binary mixture, this fact obviously suggests that the conditions for the titration of a binary mixture involving the copper(II) ion with CyDTA using the EDMA solution should be discussed from the kinetic point of view. As has been mentioned by Olson and Margerum,[6] the exchange reaction of two metal complexes generally proceeds by means of a chain-reaction mechanism. Therefore, the above reaction mechanism proposed for the reaction of the copper(II)–CyDTA complex with the metal–EDMA complex in the EDMA solution must be reasonable. Since the reactions of CyDTA with the EDMA complexes of metal(II) ions other than the nickel(II) ion in the EDMA solution proceed very rapidly, one cannot determine their reaction rates by a conventional method. Previously, the present author studied the kinetics of the substitution reaction of the nickel(II)–EDMA complex with the aminopolycarboxylate anion,[7,5b] and proposed the following reaction mechanism:

$$Ni(edma)_2^0 \rightleftharpoons Ni(edma)^+ + edma^- \qquad (4a) \text{ rapid}$$

$$Ni(edma)^+ + H_nZ^{n-m} \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} NiZ^{2-m} + H_tedma^{t-1} + (n-i)H^+ \qquad (4b)$$

He also studied the kinetics of the dissociation reaction of the nickel(II)–EDMA complex.[8] From the magnitude of their reaction rates, it was concluded that the rates of the substition and formation reactions of the nickel(II)–EDMA complex can be understood by assuming the ethylenediamine reaction mechanism[9] and the water-exchange mechanism[10,11] respectively. Furthermore, there are several features which support the conclusion that the reactions of the cadmium(II), lead(II), zinc(II), and cobalt(II) complexes also have a reaction mechanism similar to that of the corresponding reaction of the nickel(II) complex.[11,12] Therefore, it is not unreasonable to assume the ethylenediamine reaction mechanism for the CyDTA reactions of the EDMA complexes of the zinc(II), lead(II), cadmium(II), and cobalt(II) ions and the water-exchange mechanism for the formation reactions of these EDMA complexes. Thus, the relative rates for the CyDTA reactions with the EDMA complexes were calculated by assuming the ethylenediamine-reaction mechanism for the CyDTA reactions and the water-exchange mechanism for the formation reactions

of the EDMA complexes, with the aid of Eq. (5):

$$k_M = \frac{k_f'}{(1+K_2'\cdot[X]_f)} = \frac{k_M^{-H_2O}\cdot K_{OS}\cdot K_{M-gly}}{K_1\cdot(1+K_2'\cdot[X]_f)} \quad (5)$$

where all the symbols have their usual meanings.[5,11] The estimated relative k_M values for the EDMA concentration of 20 mM and the solution pH of 6.50 are listed in Table 3. Here, the steric effects of the CyDTA anion on the reaction rates are all assumed to be the same. As is shown in Table 3, the k_M values calculated for the zinc(II), cadmium(II), and lead(II) systems are much larger than that of the copper(II) system. This suggests that the equilibrium for the formation reaction of the zinc(II)-, cadmium(II)-, or lead(II)-CyDTA complex will be ensured even in the presence of the copper(II) ion. Therefore, the titration of a mixture of copper(II) and zinc(II), cadmim(II), or lead(II) can safely be discussed from the thermodynamic point of view.

Table 3. Relative rate constants for the reactions of CyDTA with metal(II)-EDMA complexes, k_M*
$[EDMA]_f=20.0$ mM, pH=6.50

System	log k_M	log $k_M^{-H_2O}$	log K_{M-gly}
Cu(II)	2.61	9.9	7.85
Ni(II)	−0.86	4.5	5.71
Cd(II)	5.47	8.3	4.65
Zn(II)	5.87	7.7	5.37
Pb(II)	6.09	8.0	5.32
Co(II)	3.72	6.0	5.08

* Rate = $k_M\cdot$[Metal(II)-EDMA]$_t\cdot$[CyDTA]

Thus, the amperometric titration (the course of which is followed by measuring the change in the concentration of the copper(II)-EDMA complex) of a mixture of copper(II) and zinc(II), cadmium(II), or lead(II) in the EDMA solution with CyDTA can be expected to give two sharp breaks. The first break corresponds to the equivalence point of zinc(II), cadmium(II), or lead(II), and the second, to that of the copper(II) ion. On the other hand, in the light of the above kinetic consideration, the k_M values for the copper(II) and nickel(II) systems evidently show that the titration of a mixture of copper(II) and nickel(II) ions in the EDMA solution will give only one end-point break, corresponding to the equivalence point of the copper(II) even when the concentration of the nickel(II) ion is 20 times higher than that of the copper(II) ion. Furthermore, as is shown by the titration curve (3) in Fig. 2, the titration of cobalt(II) in the presence of the copper(II) ion will probably give a positive error for the cobalt(II) and a negative error for the copper(II). Since the copper(II)-EDMA complex is reduced at much less negative potentials than its CyDTA complex and the EDMA and CyDTA complexes of other metal(II) ions, the above prediction was examined experimentally by following the change in the reduction wave-height of the copper(II)-EDMA complex. Some typical titration curves obtained for the Cu(II)~Zn(II) and Cu(II)~Ni(II) systems are reproduced in Fig. 4. In full accordance with the theoretical prediction, the equimolar mixture of copper(II) and zinc(II), cadmium(II), or lead(II) ions in the EDMA solution could be titrated successfully with CyDTA, and the

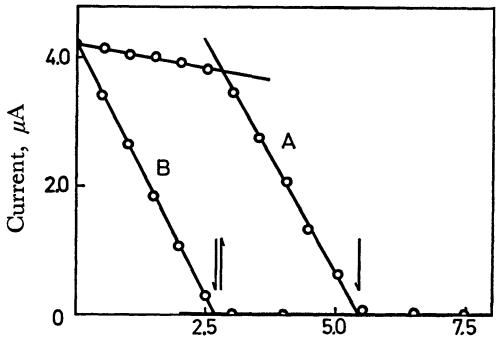

Fig. 4. Amperometric titration curves of 50 ml binary metal(II)-ion mixture with CyDTA.
$[EDMA]_f=20.0$ mM, 25 °C, $\mu=0.30$
[CyDTA]=19.2 mM, pH=6.30
A) [Cu(II)]=1.02 mM, [Zn(II)]=1.07_5 mM
B) [Cu(II)]=1.02 mM, [Ni(II)]=20.0 mM

Table 4. Amperometric titration of a binary metal-ion mixture with CyDTA
$\mu=0.30$, 25 °C, $[EDMA]_f=20$ mM
sample solution: 50.0 ml

A) Cu(II)~Zn(II) mixture

[Cu(II)] mM	[Zn(II)] mM	[CyDTA] mM	Equivalence point, ml Zn(II) Obsd	Zn(II) Calcd	Cu(II) Obsd	Cu(II) Calcd
1.02	4.30	76.8	2.76	2.80	0.67	0.66_5
1.02	2.15	38.4	2.78	2.80	1.33	1.33
1.02	0.53_8	19.2	2.76	2.80	2.66	2.65
2.04	1.07_5	38.4	1.39	1.40	2.66	2.65
1.02	1.07_5	19.2	2.78	2.80	2.66	2.65
0.51_0	1.07_5	19.2	2.81	2.80	1.32	1.33

B) Cu(II)~Ni(II) mixture

[Cu(II)] mM	[Ni(II)] mM	[CyDTA] mM	Equivalence point, ml Cu(II) Obsd	Cu(II) Calcd
1.02	22.0	19.2	2.63	2.65
1.02	5.50	19.2	2.64	2.65
1.02	1.10	19.2	2.64	2.65
1.02	0.55	19.2	2.65	2.65
0.20_4	11.0	3.84	2.68	2.65

C) Cu(II)~Co(II) mixture

[Cu(II)] mM	[Co(II)] mM	[CyDTA] mM	Equivalence point, ml Cu(II) Obsd	Cu(II) Calcd	Co(II) Obsd	Co(II) Calcd
0.51_0	3.73	38.4	0.43	0.44_4	3.60	3.57
1.02	0.91_1	19.2	2.60	2.65	2.43	2.38
1.02	0.91_1	9.60	5.14	5.30	2.54	2.38
2.04	0.45_6	19.2	5.22	5.30	1.27	1.19

nickel(II) ion had no effect on the amperometric determination of copper(II) (Table 4). The amperometric titration of a binary mixture of the nickel(II) ion and the lead(II), cadmium(II), or cobalt(II) ion with CyDTA was also carried out in the EDMA solution. The nickel(II) had no effect on the determination of lead(II), cadmium(II), or cobalt(II) with CyDTA. This can be also be ascribable to the inertness of the CyDTA reaction of the nickel(II)–EDMA complex. As is shown by the data in Table 4, the CyDTA titration of a mixture of copper(II) and cobalt(II) ions, especially when the concentration of copper(II) ions is high, gave a positive error for the cobalt(II) determination. This is in good accordance with the theoretical prediction made from the kinetic point of view. The K'_{MZ} values in Table 1 evidently show that, thermodynamically, the successful determination of cobalt(II) in the presence of copper(II) is possible.

The present author also investigated the amperometric titration of a mixture of copper(II) and nickel(II) ions in the EDMA solution, using DTPA as a titrant. As in the case of the CyDTA system, the K'_{MZ} value for the nickel(II) ion is much larger than that of the copper(II) ion, but the k_M value for the copper(II)–EDMA∼DTPA reaction can be expected to be much larger than that of the nickel(II)–EDMA∼DTPA reaction, suggesting the possibility of the successful performance of the selective titration of copper(II). However, no distinct end break could be obtained. This can probably be ascribed to the fact that the reaction of the copper(II)–DTPA complex with the nickel(II)–EDMA complex in the EDMA solution proceeds to an appreciable extent.

This paper has been concerned only with the amperometric titration of binary metal-ion mixtures in an EDMA solution with CyDTA, because the kinetics of this system could be fully investigated. However, many other systems can probably be submitted to the titration of multicomponent mixtures.

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