

A Flow Injection/Stopped-flow Kinetic Study of the Ligand Substitution of Europium(III) Complex with Thenoyltrifluoroacetone and Trioctylphosphine Oxide by Aminopolycarboxylic Acids

Makoto Aihara,* and Naomi Mori

*Faculty of Home Life Science, Fukuoka Women's University,
Higashi-ku, Kasumigaoka, Fukuoka 813, Japan*

ABSTRACT

The ligand substitution of europium(III) complex with thenyltrifluoroacetone(TTA) and trioctylphosphine oxide(TOPO) by aminopolycarboxylic acid(ethylenediaminetetraacetic acid (EDTA) or trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid(CyDTA)) in non-ionic surfactants was investigated by flow injection/stopped-flow method. By analyzing the decrease of fluorescence of $\text{Eu}(\text{TTA})_3(\text{TOPO})_2$, the substitution rate was found to be a first-order rate law with respect to the concentration of $\text{Eu}(\text{TTA})_3(\text{TOPO})_2$. The pH dependence of the rate constants can be explained by the mechanism of the rate determination step.

INTRODUCTION

Spectrofluorimetric determination of europium(III), terbium(III) and samarium(III) on solubilizing the complexes with β -diketone and TOPO in micellar solution has been reported.¹⁻³⁾ The technique based on solubilizing complex

in non-ionic surfactant has been applied to flow injection analysis of europium(III), samarium(III) and terbium(III).⁴⁻⁶⁾

In this paper, the substitution of europium(III) complex with thenyltrifluoroacetone and trioctylphosphine oxide by ethylenediaminetetraacetic acid and 1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid in micellar solution.

EXPERIMENTAL

Stock solutions of mixed ligands(TTA and TOPO) were prepared by dissolving the reagents(Dojindo Laboratories) in an aqueous solution of non-ionic surfactant. The surfactants were BL-9EX; $\text{CH}_3(\text{CH}_2)_{11}-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_9\text{H}$, Emulgen 120; $\text{CH}_3(\text{CH}_2)_{11}-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_{13}\text{H}$ and Triton X-100; $(\text{CH}_3)_2\text{CCH}_2\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ($n = 9-10$). The chelating agents used were ethylenediaminetetraacetic acid (EDTA) and trans-1,2-cyclohexanediamine-N,N,N',N'-tetraacetic acid(CyDTA).

The flow injection system is shown in Fig. 1. Detector was a spectrofluorimeter(UVIDIC-610, Japanspectroscopic Co.) with a flow cell(32 μl).

For the stopped-flow method, the stopped-flow valve(T_1) was switched to lead the carrier solution to waste(W) and to stop the sample zone in the flow cell. Kinetic studies of the Eu(III) system was carried out on the method. The fluorescence was measured at apparent excitation and emission wave lengths of 352 and 613 nm, respectively. The substitution of TTA-TOPO from its Eu(III) complex by an aminopolycarboxylic acid is characterized by a decrease in fluorescence at 613 nm.

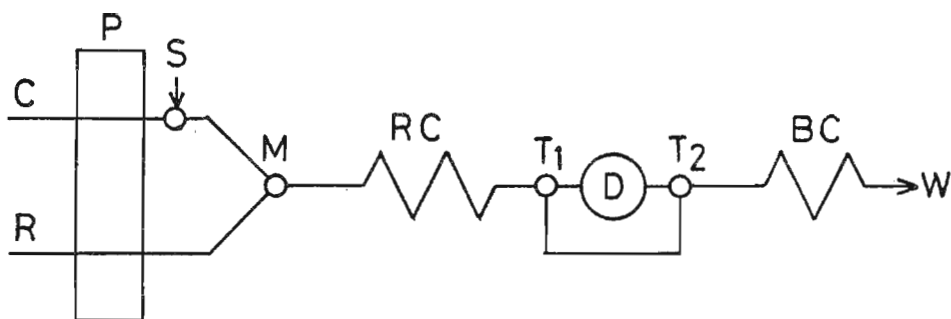
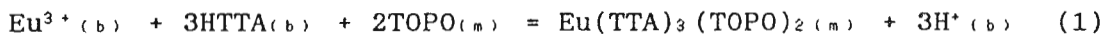


Fig. 1. Flow manifold. C, 0.5 % surfactant and acetate buffer solution; R, Eu(III)-TTA-TOPO, 0.5 % surfactant and buffer solution; S, sample injection(100 μ l); M, mixing joint; RC, reaction coil; T₁, stopped-flow valve; T₂, three way joint; D, detector; BC, back pressure coil(1m); P, pump and W, waste.

RESULTS AND DISCUSSION

It was recognized by a spectrophotometric method that most of TTA exists outside the micelle. On the other hand, Eu(III)-TTA and europium(III)-TTA-TOPO complexes were found to exist in the micellar solution.

The following equilibrium for Eu(III)-TTA-TOPO system was postulated in a micellar solution¹⁻³⁾



Where the subscripts(b) and (m) refer to mutually equilibrated bulk and micellar phases, respectively.

The substitution of TTA and TOPO from its europium(III) complexes by a chelating agent was investigated with flow injection/stopped-flow method. The effect of different surfactants and pH on the stopped-flow pattern of these systems was

investigated. Fig. 2 shows typical example of substitution reaction curves for Eu(III)-TTA-TOPO-EDTA and Eu(III)-TTA-TOPO-CyDTA systems.

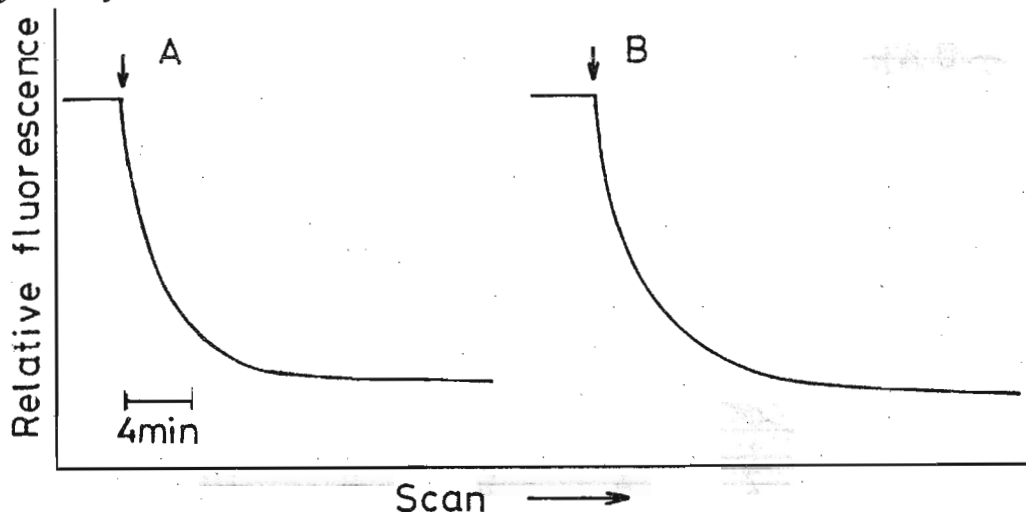


Fig. 2. Stopped-flow signals obtained with the flow system in aqueous solution of BL-9EX. A, Eu(III)-TTA-TOPO-EDTA system. $[Eu(III)] = 8 \times 10^{-6}$ M, $[EDTA] = 8 \times 10^{-5}$ M, pH = 4.25 ; B, Eu(III)-TTA-TOPO-CyDTA system. $[Eu(III)] = 8 \times 10^{-6}$, $[CyDTA] = 8 \times 10^{-5}$ M, pH = 4.25

The $\log (A_0 - A)$ plots against time are shown for the systems of Eu(III)-TTA-TOPO-EDTA, and Eu(III)-TTA-TOPO-CyDTA in BL-9EX in Fig. 3. The linearity of the plots showed first-order law with respect to the $Eu(TTA)_3(TOPO)_2$

The apparent first order rate constants, $k \text{ sec}^{-1}$, were determined by using a Kezoly-Swinbourne plot.^{7,8} The rates of the substitution reactions were measured at pH 3.50 - 5.00 in solutions of various non-ionic surfactants. The rate constants for these systems are given in Table 1-2. Hydrogen ion dependence of the reactions are shown in Fig. 4. These plots show a first order hydrogen ion dependence.

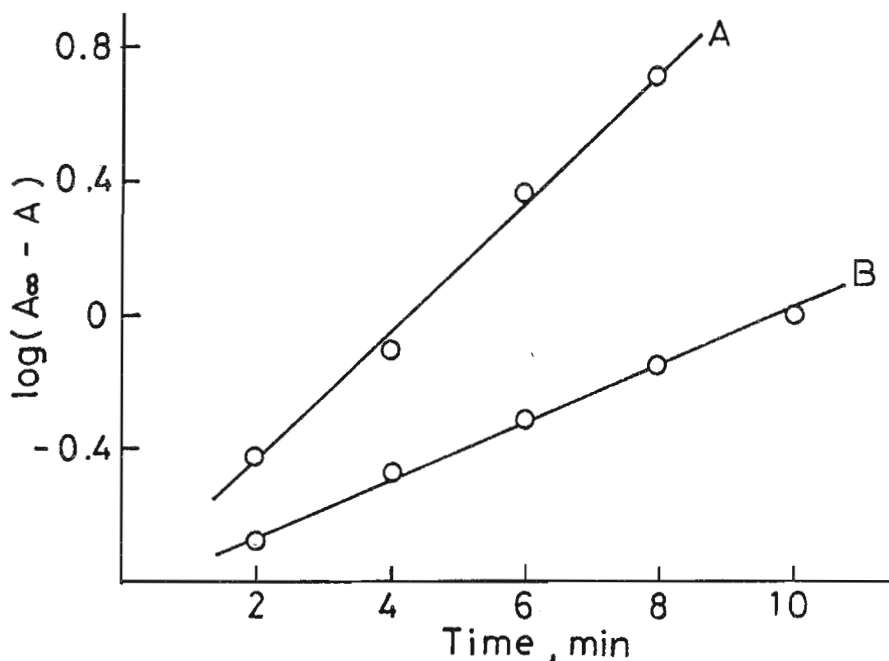


Fig. 3. First-order rate plots for the substitution reactions in aqueous solutions of BL-9EX. A, $[\text{Eu(III)}] = 8 \times 10^{-6} \text{ M}$, $[\text{EDTA}] = 8 \times 10^{-5} \text{ M}$, $\text{pH} = 4.25$; B, $[\text{Eu(III)}] = 8 \times 10^{-6} \text{ M}$, $[\text{CyDTA}] = 8 \times 10^{-5} \text{ M}$, $\text{pH} = 4.25$.

Table 1. Rate constants for the ligand substitution reactions. (I)Eu(III)-TTA-TOPO-EDTA system (II)Eu(III)-TTA-TOPO-CyDTA system in BL-9EX solution in BL-9EX solution

pH	k_1	k_2	pH	k_1	k_2
	10^{-3} sec^{-1}				
4.00	10.5	11.8	4.00	8.6	11.0
4.25	7.9	9.2	4.25	5.4	7.6
4.50	5.1	7.2	4.50	3.2	4.6
5.00	4.4	6.3	5.00	2.1	2.7

$k_1 : 8 \times 10^{-5} \text{ M}$, $k_2 : 1.6 \times 10^{-4} \text{ M}$.

Table 2. Rate constants for the ligand substitution reactions.

(I)Eu(III)-TTA-TOPO-EDTA system (II) Eu(III)-TTA-TOPO-EDTA

in Emulgen 120 solution

system in Triton X-100 solution

pH	k ₁	k ₂	pH	k ₁	k ₂
	10 ⁻³ sec ⁻¹				
4.00	11.0	12.1	3.50	5.2	5.4
4.25	9.8	10.1	3.75	4.0	4.3
4.50	7.6	8.2	4.00	1.8	2.6
5.00	5.3	5.9	4.25	0.78	0.83

k₁ : 8 X 10⁻⁵ M, k₂ : 1.6 x 10⁻⁴ M.

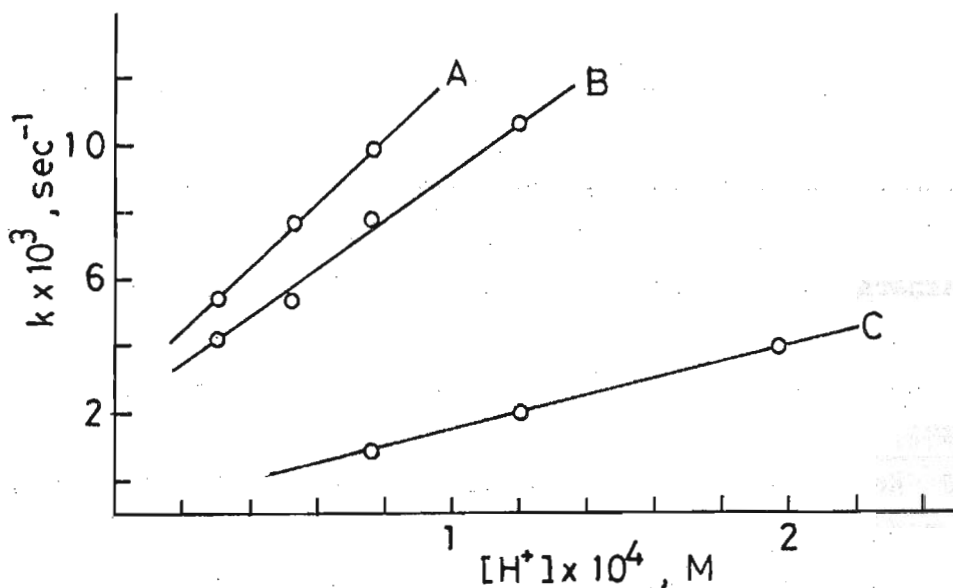
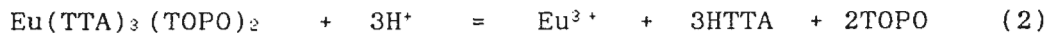


Fig. 4. Hydrogen ion dependence of the observed first-order rate constants in aqueous solutions of (A) Emulgen 120, (B) BL-9EX and (C) Triton X-100. [Eu(III)] = 8 X 10⁻⁶ M, [EDTA] = 8 X 10⁻⁵ M.

The mechanism of the ligand substitution reactions is assumed to be as follows



where L^{n-} is EDTA or CyDTA anion. The rate-determination step is assumed to be Reaction (2).

The rates were found to be almost same in aqueous solutions of BL-9EX and Emulgen 120 which have same structure. The rates in aqueous solutions of BL-9EX and Emulgen 120 were very fast compared with those in an aqueous solution of Triton X-100.

REFERENCES

1. T. Taketatsu and A. Sato, *Anal. Chem. Acta*, 108, 429(1979).
2. T. Taketatsu, *Chem. Lett.*, 1057(1981).
3. T. Taketatsu, *Talanta*, 29, 397(1982).
4. M. Aihara, M. Arai and T. Taketatsu, *Analyst*, 111, 641(1989).
5. M. Aihara, M. Arai and T. Taketatsu, *Anal. Lett.*, 19, 1907(1986).
6. M. Aihara and T. Nakasimada, *J. Flow Injection Anal.*, 6, (1989).
7. F. J. Kezdy, J. Jaz and A. Bruylants, *Bull. Soc. Chim. Belg.*, 67, 689(1958).
8. E. Swinbourne, *J. Chem. Soc.*, 2371(1960).

(Accepted 15 May 1991)