



Title	Effect of a Quaternary Ammonium Base on the Extraction Rate of Beryllium-Thenoyltrifluoroacetone Chelate
Author(s)	NORIKI, Shinichiro; 乗木, 新一郎
Citation	北海道大學水産學部研究彙報, 35(1), 43-49
Issue Date	1984-03
Doc URL	https://hdl.handle.net/2115/23847
Type	departmental bulletin paper
File Information	35(1)_P43-49.pdf



Effect of a Quaternary Ammonium Base on the Extraction Rate of Beryllium-Thenoyltrifluoroacetone Chelate

Shinichiro NORIKI*

Abstract

Effect of a quaternary ammonium base, zephiramine, on the kinetics and mechanism of the extraction of beryllium with thenoyltrifluoroacetone (TTA) was studied. The composition of the ordinary TTA chelate (Be: TTA=1:2) was not affected by the addition of zephiramine. The reaction orders with respect to beryllium, TTA, and pH in the presence of zephiramine were found to be unity, and the zephiramine dependency zero. The presence of zephiramine does not affect the formation and extraction mechanism of the Be-TTA chelate, but the apparent extraction rate of the chelate was enhanced 1.5 times by the presence of zephiramine.

Introduction

In a previous paper¹⁻⁶, the author reported that a coordination-unsaturated chelate changes to a coordination-saturated chelate in the presence of a quaternary ammonium base, and suggested that a quaternary ammonium base attacks the coordinated water molecules of a metal chelate.

The extraction of beryllium with thenoyltrifluoroacetone (TTA) occurs very slowly from an acid solution.⁷ In the extraction system, the rate-determining step is the reaction forming the mono-ligand chelate and related to the dissociation of the coordinated water of the metal ion,^{8,9} namely the rupture of metal-water bonds. The smaller the value of the rate constant for water dissociation is, the slower the reaction time will be. The extraction of beryllium with TTA is a typical case of a slow reaction.

In this paper, the kinetics and mechanism of chelate formation of beryllium with TTA in the presence of a quaternary ammonium base are investigated. As a representative of a quaternary ammonium base, tetradecyldimethylbenzylammonium chloride, so-called zephiramine (Zeph or Z), was chosen.

Experimental

Reagents

Beryllium solution, 1×10^{-2} M. Dissolve 1.77 g of beryllium sulfate in 1 l of water.

Zephiramine solution, 5×10^{-3} M. Dissolve 0.920 g of tetradecyldimethylbenzylammonium chloride in 500 ml of water.

TTA solution, 1×10^{-2} M. Dissolve 1.11 g of thenoyltrifluoroacetone in 500 ml

* *Laboratory of Analytical Chemistry, Faculty of Fisheries, Hokkaido University*
(北海道大学水産学部分析化学講座)

of benzene.

Buffer solution. The pH of a solution was adjusted with acetate buffer.

Redistilled water was used throughout the study.

All the chemicals used were of analytical-reagent grade.

Procedure

The beryllium, acetate buffer and zephiramine solutions were placed in a separatory funnel, and diluted to 20 ml with water. The initial aqueous beryllium concentration in all cases was 1×10^{-4} M. The aqueous solution was shaken for a definite time interval with a benzene solution of TTA. Following agitation, the solution was allowed to stand until phase separation had occurred. The pH of the aqueous phase was determined with a pH-meter after the agitation.

The per cent extracted was obtained by determining the beryllium concentration in the aqueous phase by colorimetry using cromazurol S.¹⁰⁾

All extractions were done in a thermostated room ($25 \pm 1^\circ\text{C}$).

Results and Discussion

In solvent extraction of a metal chelate, the reaction order with respect to the metal ion (M) can be determined from plots of $\log [M]_{t=0} / [M]_{t=t}$ vs. time, [M] being the concentration in the aqueous phase. The results for extraction of beryllium with TTA are shown in Fig. 1. These plots gave straight lines indicative of a first-order reaction with respect to beryllium ion in both the absence and presence of zephiramine, and showed that the extraction rate is increased by the presence of zephiramine.

At various conditions of the variables, i.e. TTA, pH and zephiramine (zeph), all plots gave straight lines and showed the increment of the extraction rate by

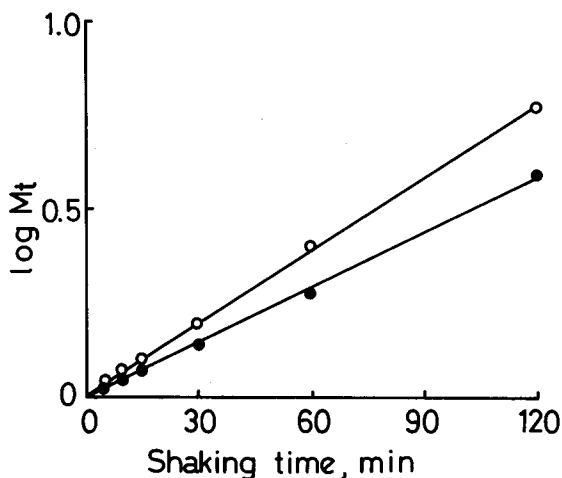


Fig. 1. Reaction order of Be^{2+} in Be-TTA chelate formation. $[\text{TTA}] = 1 \times 10^{-2}$ M, pH 3.76, and $[\text{Z}] = \bullet - 0$ M and $\circ - 5 \times 10^{-4}$ M. $M_t = [\text{Be}^{2+}]_{t=0} / [\text{Be}^{2+}]_{t=t}$.

NORIKI: Quaternary Ammonium Base on the Extraction

Table 1. Kinetic data for extraction of beryllium with TTA.

TTA M	Zeph M	pH	log M _t *					k** 10 ⁻⁴
			Shaking time, min					
			5	10	15	30	60	
1×10 ⁻³	0	4.00	1.020	1.031	1.042	1.053	1.075	2.11
"	5.0×10 ⁻⁴	"	1.047	1.087	1.099	1.149	1.205	2.37
2×10 ⁻³	0	"	1.020	1.042	1.064	1.099	1.149	0.84
"	5.0×10 ⁻⁴	"	1.099	1.111	1.163	1.250	1.515	3.06
3×10 ⁻³	0	"	1.053	1.064	1.099	1.124	1.299	1.85
"	5.0×10 ⁻⁴	"	1.124	1.163	1.220	1.389	1.818	2.99
5×10 ⁻³	0	"	1.031	1.031	1.099	1.220	1.587	1.38
"	5.0×10 ⁻⁴	"	1.087	1.176	1.266	1.563	2.439	2.84
1×10 ⁻²	0	"	1.020	1.136	1.282	1.754	2.381	1.36
"	5.0×10 ⁻⁴	"	1.190	1.3899	1.667	2.632	6.896	3.22
1×10 ⁻²	0	3.15	1.000	1.000	1.000	1.036	1.117	2.00
"	5.0×10 ⁻⁴	"	1.000	1.042	1.058	1.176	1.333	3.13
"	0	3.45	1.042	1.075	1.087	1.170	1.429	1.98
"	5.0×10 ⁻⁴	"	1.087	1.124	1.227	1.342	1.724	2.59
"	0	3.76	1.020	1.093	1.156	1.370	1.887	2.00
"	5.0×10 ⁻⁴	"	1.075	1.176	1.299	1.626	2.500	2.63
"	0	4.10	—	—	1.389	2.222	6.896	2.50
"	5.0×10 ⁻⁴	"	—	—	2.041	3.030	12.500	3.32
"	0	4.35	1.250	1.574	2.041	4.000	—	2.09
"	5.0×10 ⁻⁴	"	1.575	2.000	2.381	5.263	—	2.40
"	2.0×10 ⁻⁵	4.00	1.053	1.205	1.389	2.041	—	2.65
"	5.0×10 ⁻⁵	"	1.087	1.250	1.493	2.326	—	3.03
"	1.0×10 ⁻⁴	"	1.099	1.333	1.613	2.564	—	3.39
"	2.5×10 ⁻⁴	"	1.190	1.389	1.667	2.632	—	3.17
"	1.0×10 ⁻⁴	"	1.250	1.493	1.852	2.632	—	3.50

$$* M_t = [M]_{t=0} / [M]_{t=t}$$

$$** k \text{ (min}^{-1}\text{)} = (\Delta \log M_t / \Delta t) \times 2.303 \times \frac{[H^+]}{[HA]_{org}}$$

zephiramine (Table 1).

To make the role of zephiramine clear, the author examined the effect of zephiramine on the reaction order with respect to the variables and the composition of the extracted chelate. Dependences of log S, S being $\Delta \log M_t / \Delta t$ (Table 1), on log [TTA], pH and log [Zeph] give the reaction order with respect to TTA (Fig. 2), pH (Fig. 3) and zephiramine (Fig. 4), respectively. Results shown in Figs. 2-4 indicate that the reaction is the first-order with respect to TTA and pH, and zephiramine has no effect on the reaction order of this extraction system.

The method of equilibrium shift suggests that the extracted beryllium chelate has the composition Be[TTA]₂, and the extracted chelate has no zephiramine in its composition in the presence of zephiramine (Figs. 5-7).

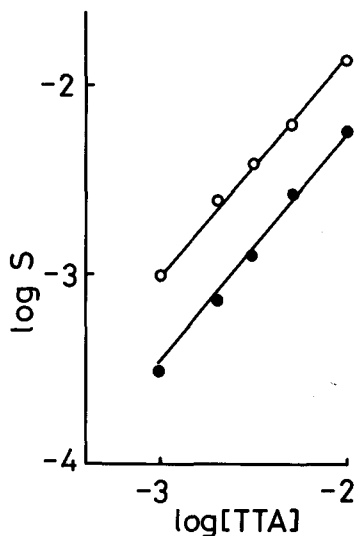


Fig. 2. Reaction order of TTA in Be-TTA chelate formation. pH 4.00, and $[Z] =$ —●— 0 M and —○— 5×10^{-4} M.

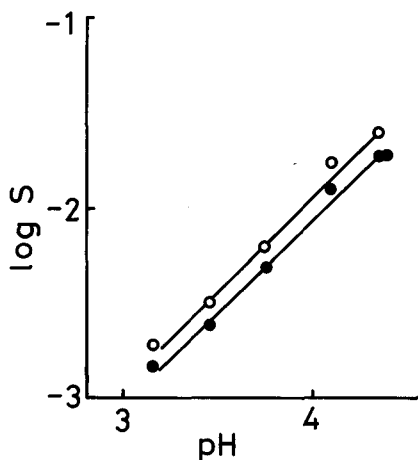


Fig. 3. Reaction order of pH in Be-TTA chelate formation. $[TTA] = 1 \times 10^{-2} \text{ M}$, and $[Z] =$ —●— 0 M and —○— 5×10^{-4} M.

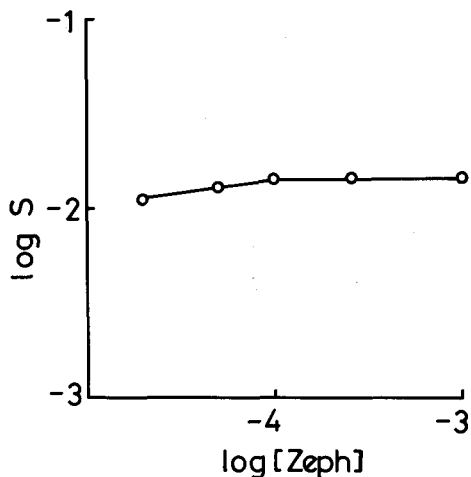


Fig. 4. Reaction order of zephiramine in Be-TTA chelate formation. $[TTA] = 1 \times 10^{-2} \text{ M}$, and pH 4.00.

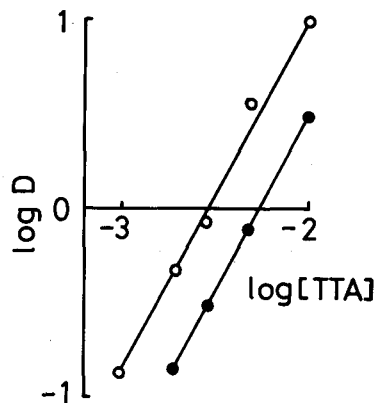


Fig. 5. Dependency of distribution ratio of Be-TTA chelate upon TTA. pH 4.00, and $[Z] =$ —●— 0 M and —○— 5×10^{-4} M. Shaking time 60 min.

From the results mentioned above, the author concluded that the extraction rate is increased by zephiramine but that the latter does not cause a change of mechanism of chelate formation and extraction.

In metal-chelation, the rate-determining step is the reaction forming the mono-

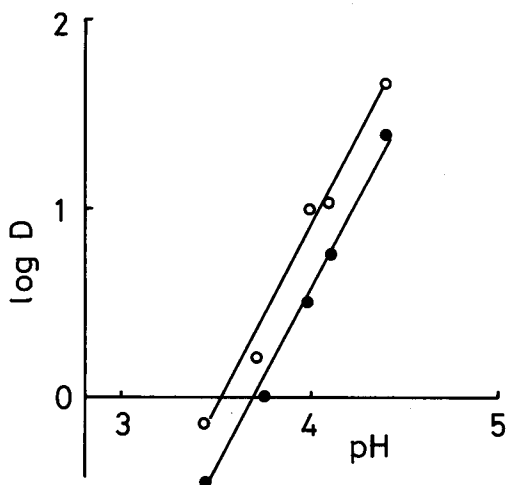


Fig. 6. Dependency of distribution ratio of Be-TTA chelate upon pH. $[TTA] = 1 \times 10^{-2}$ M, and $[Z] = \bullet - 0$ M and $\circ - 5 \times 10^{-3}$ M. Shaking time 60 min.

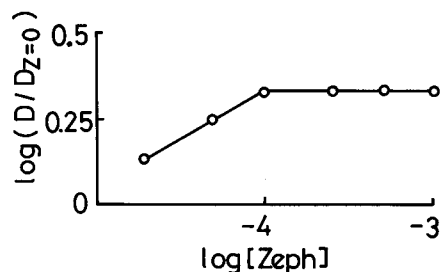


Fig. 7. Dependency of distribution ratio of Be-TTA chelate upon Zephiramine. $[TTA] = 1 \times 10^{-2}$ M and pH 4.00. Shaking time 30 min.

ligand chelate, and the rate of extraction can be shown to obey the rate expression :

$$-\frac{d[Be^{2+}]}{dt} = k \times \frac{[Be^{2+}][HA]_{org}}{[H^+]}$$

k can be calculated from the data on $\log M_e$. The mean values of $k(\text{min}^{-1})$ are $(1.81 \pm 0.48) \times 10^{-4}$ and $(2.95 \pm 0.35) \times 10^{-4}$ in the absence and the presence of zephiramine, respectively. The value of k in the presence of zephiramine is thus 1.5 times that in its absence.

Here, k indicates the over-all extraction rate. Hence, the rate constant of the rate-determining step,

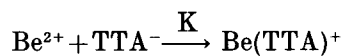


Table 2. Comparison of rate for over all extraction (k) with rate constant for mono-ligand formation in the presence of zephiramine.

Zeph, M	pK_a^*	K_D^*	k (min^{-1})	K ($M^{-1} \cdot \text{min}^{-1}$)
0	6.30	40	1.81	1.44×10^4
1.0×10^{-4}	6.30	40	2.95	2.36×10^4
2.0×10^{-4}	6.30	40	2.95	2.36×10^4
2.5×10^{-4}	6.05	40	2.95	1.33×10^4
5.0×10^{-4}	5.55	40	2.95	4.22×10^3
1.0×10^{-4}	4.80	40	2.95	7.50×10^2

* Refs. 11-14 and this work.

will be expressed as follows :

$$K = k \times \frac{K_D}{K_a}$$

where, K_D is the partition coefficient of TTA between benzene and the aqueous phase and K_a is the acid dissociation constant of TTA. As listed in Table 1, the apparent dissociation constant, k , increased by zephiramine which was more than 2.0×10^{-4} M. K was calculated by using the results shown in Table 1 (Table 2). The apparent extraction rate was increased by zephiramine, but the rate-determining reaction (K) was inhibited at a concentration of zephiramine more than 2×10^{-4} M.

Zephiramine is a surface active agent having a positive charge and high molecular weight. Thus, zephiramine has a structure-breaking property at a concentration less than the critical micelle concentration, approximately 2×10^{-4} M,¹⁵⁾ but it has a structure-forming property after a micelle is formed. Structure-breaking property enhances the dissociation of the coordinated water, and gives a large K value, while the structure-forming property will give the opposite result.

From the results presented here, it may be concluded that zephiramine has an effect of increasing the apparent extraction rate of beryllium with TTA, and K is either increased by the structure-breaking property of zephiramine, or is decreased by the structure-forming property of zephiramine at more than 2×10^{-4} M.

Acknowledgements

I wish to thank emeritus Prof. M. Nishimura for his valuable advice and discussions. Thanks are given to Dr. S. Tsunogai and the members of the Laboratory of Analytical Chemistry of this faculty for their encouraging discussions.

References

- 1) Nishimura, M., Noriki, S. and Muramoto, S. (1974). Effect of quaternary ammonium bases on valence-saturated but coordination-unsaturated chelates. Part I. Extraction of chelates of glyoxal bis-(2-hydroxyanil) and o-(salicylideneamino)phenol. *Anal. Chim. Acta* **70**, 121-126.
- 2) Noriki, S. and Nishimura, M. (1974). *Ditto*, Part II. Extraction of magnesium 8-hydroxyquinolate. *Ibid.* **72**, 339-343.
- 3) Noriki, S. (1975). *Ditto*, Part III. Extraction of nickel- and cobalt-thenoyltrifluoroacetone chelates. *Ibid.* **76**, 215-218.
- 4) Noriki, S. and Nishimura, M. (1977). *Ditto*, Part IV. Extraction of some divalent metal 8-hydroxyquinoline. *Ibid.* **94**, 57-62.
- 5) Nishimura, M. and Noriki, S. (1975). Effect of a quaternary ammonium base on chelate formation. *Anal. Instruments* **13**, 24-31. (In Japanese).
- 6) Noriki, S. (1983). Adductive effect of a quaternary ammonium base on solvent extraction of coordination-unsaturated chelates. *Bull. Fac. Fish. Hokkaido Univ.* **34**, 264-277. (In Japanese with English abstract).
- 7) Bolomey, R.A. and Wish, L. (1950). Thenoyltrifluoroacetone as a complexing agent for the isolation and purification of carrier-free radioberyllium. *J. Amer. Chem. Soc.* **72**, 4483-4486.
- 8) McClellan, B.E. and Freiser, H. (1964). Kinetics and mechanism of extraction of zinc, nickel, cobalt, and cadmium with diphenylthiocarbazono, di-o-tolylthiocarbazono, and di- α -naphthylthiocarbazono. *Anal. Chem.* **36**, 2262-2265.
- 9) McClellan, B.E. and Menis, O. (1971). Kinetics and mechanism of extraction of iron (III) with β -isopropyltropolone. *Ibid.* **43**, 436-438.
- 10) Horiuchi, Y. and Nishida, H. (1969). Spectrophotometric determination of beryllium with

NORIKI : Quaternary Ammonium Base on the Extraction

- chromazurol S and zephiramine. *Bunseki Kagaku* **18**, 180-184. (In Japanese with English abstract).
- 11) King, E.L. and Reas, W.H. (1951). The activity coefficient of thenoyltrifluoroacetone in benzen solution. *J. Amer. Chem. Soc.* **73**, 1804-1805.
 - 12) Cook, E.H. and Taft, R.M. (1952). Concerning the behavior of aqueous thenoyltrifluoroacetone. *Ibid.* **74**, 6103-6104.
 - 13) Reid, J.C. and CALVIN, M. (1950). Some new β -diketones containing the trifluoromethyl group. *Ibid.* **72**, 2948-2952.
 - 14) Stary, J. (1964). *Solvent extraction of metal chelate*. 240 p. Pergamon, Oxford.
 - 15) Ueno, K. (1971). Application of cationic surfactants in analytical chemistry. *Bunseki Kagaku* **20**, 736-748. (In Japanese).