Bull. Inst. Chem. Res., Kyoto Univ., Vol. 55, No. 5, 1977

Extraction Behavior of Metal Benzoyltrifluoroacetonates

Takaharu HONJO†, Masakazu MATSUI, and Tsunenobu SHIGEMATSU*

Received June 23, 1977

The behavior of trace amounts of iron, cobalt, copper, zinc, indium, uranium, zirconium, scandium, lanthanum, cerium, neodymium, samarium, europium, terbium, ytterbium, and lutetium in solvent extraction has been reviewed in order to ascertain the basic conditions for the separation of metals as their benzoyltrifluoroacetonates by solvent extraction. The pH of the half extraction decreases in the following order: Co(II)–Zn(II)–La(III)–Nd(III)–Ce(III)–Eu(III)–Tb(III)–Sm(III)–Yb(III)–Lu(III)–In(III)–UO_2(II)–Fe(III)–Sc(III)–Cu(II)–Zr(IV). The extraction constants for the benzoyltrifluoroacetonate chelates tend to increase with an increase in the ionic potential of the metals. The variation of the extraction constants of rare earth chelates with atomic number of rare earth elements shows interesting tetrad effects.

INTRODUCTION

In recent years, the liquid-liquid extraction of metals with various β-diketones has been reported and reviewed,[1] however, benzoyltrifluoroacetone has scarcely yet been used for the extraction separation of various metals. In this article, the behavior of trace amounts of iron (III), cobalt (II), copper (II), zinc (II), indium (III), uranium (VI), zirconium (IV), scandium (III), lanthanum (III), cerium (III), neodymium (III), samarium (III), europium (III), terbium (III), ytterbium (III), and lutetium (III), in solvent extraction has been reviewed in order to ascertain the basic conditions for the separation of metals as their benzoyltrifluoroacetonates by solvent extraction.

EXPERIMENTAL

The benzoyltrifluoroacetone (white needle crystal, m.p. 39–41°C, b.p. 224°C) was supplied from the Dojindo Co., Ltd., Research Laboratories. Reagent-grade benzene was used without further purification. The experimental procedures were already described in the previous papers.[2,3,4,6,8,10] In general, the extractions were carried out between 10 ml of a buffered solution containing trace amounts of metal ions and the same volume of an organic solution containing 0.05 M benzoyltrifluoroacetone in benzene. The aqueous solution was made to have 0.01–0.1 M acetic acid (in the acidic region) or 0.01–0.1 M boric acid (in the basic region), and its pH was adjusted to an appropriate value. The two phases were shaken by means of a mechanical shaker for 30 min to one hour at room temperature (20–25°C). After centrifugation, the distribution of the metals was determined radiometri-

* 本浄高治, 松井正和, 重松恒信: Laboratory of Radiochemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto 611.

† Present address: Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa, Ishikawa 920.

cally for cobalt (Co–60), zinc (Zn–65), zirconium (Zr–95), scandium (Sc–46), lanthanum (La–140), cerium (Ce–144), neodymium (Nd–147), samarium (Sm–145), europium (Eu–152, 154), terbium (Tb–160), ytterbium (Yb–169), and lutetium (Lu–177), spectrophotometrically for iron and uranium as their benzoyltrifluoroacetonates,[3] polarographically for copper as well as fluorometrically for indium as its 2-methyloxinate,[4] respectively. The pH of the aqueous phase was checked again after extraction with use of the pH meter.

THEORETICAL

The percentage of extraction, $\%E$, the extraction constant of a metal chelate, K, and the pH of the half extraction, $pH_{1/2}$, can be calculated from the data obtained by the following equations:

$$D=(MR_n)_O/(M^{n+}) \quad (1)$$

$$\%E=100D/(1+D) \quad (2)$$

$$K=(MR_n)_O(H^+)^n/(M^{n+})(HR)_O^n \quad (3)$$

$$\log K=\log D-n\log(HR)_O-n\,pH \quad (4)$$

$$pH_{1/2}=-\log K/n-\log(HR)_O \quad (5)$$

where D is the net distribution ratios of a metal in the extraction; M stands for metal, and HR for benzoyltrifluoroacetone; the parentheses designate the concentration of the chemical species in the aqueous phase and in the organic phase with the suffix O.

RESULTS AND DISCUSSION

The extraction of trace amounts of 16 metals with 0.05 M benzoyltrifluoroacetone in benzene was investigated for various acidic and basic aqueous solutions. The results are shown in Figs. 1–2 as a function of the pH or H_2SO_4(M) of the aqueous phase. The data on the logarithm of the extraction constant, $\log K$, and the $pH_{1/2}$ values of metal benzoyltrifluoroacetonates obtained in the present extraction system are summarized in Table I. The values in $pH_{1/2}$ decrease in the following order: Co(II)–Zn(II)–La(III)–Nd(III)–Ce(III)–Eu(III)–Tb(III)–Sm(III)–Yb(III)–Lu(III)–In(III)–UO_2(II)–Fe(III)–Sc(III)–Cu(II)–Zr(IV). The free energy of the formation of a complex between a metal ion and an

Table I. Extraction Constant, $\log K$, and pH of the Half Extraction, $pH_{1/2}$, Determined by the Extraction of Metals with 0.05 M Benzoyltrifluoroacetone in Benzene

Metal ion	log K	$pH_{1/2}$	Metal ion	log K	$pH_{1/2}$
Fe(III)	−2.31	2.07	La(III)	−11.6	5.17
Co(II)	−8.60	5.60	Ce(III)	−9.5	4.47
Cu(II)	−1.26	1.93	Nd(III)	−9.9	4.60
Zn(II)	−8.56	5.58	Sm(III)	−8.1	4.00
In(III)	−6.36	3.42	Eu(III)	−8.9	4.27
UO_2(II)	−3.40	3.00	Tb(III)	−8.8	4.23
Zr(IV)		1M H_2SO_4	Yb(III)	−7.8	3.90
Sc(III)	−1.40	1.77	Lu(III)	−7.7	3.87

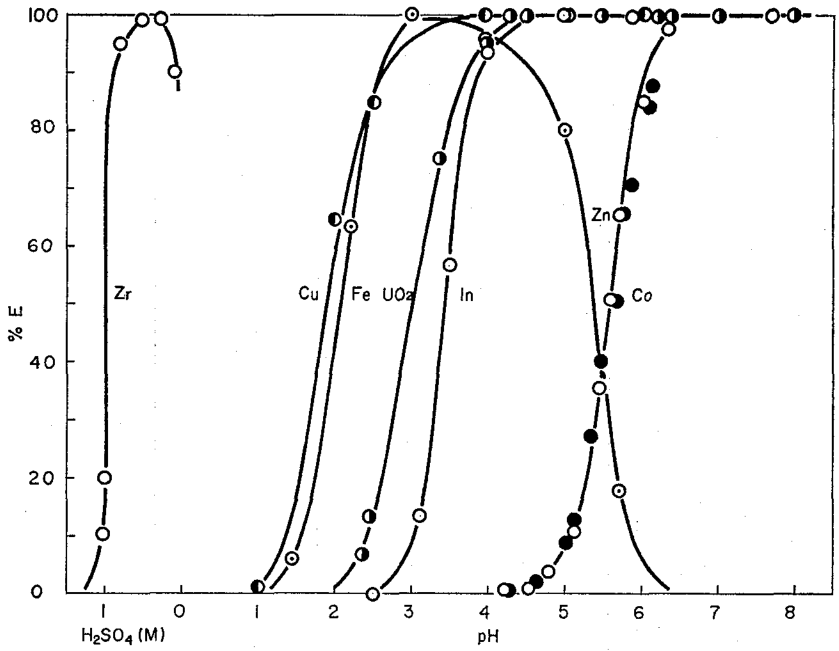

Fig. 1. The effect of pH or H_2SO_4 (M) on the extraction of trace amounts of Co(II), Cu(II), Fe(III), In(III), UO_2(II), Zn(II), and Zr(IV)–0.05 M benzoyltrifluoroacetone-benzene system.

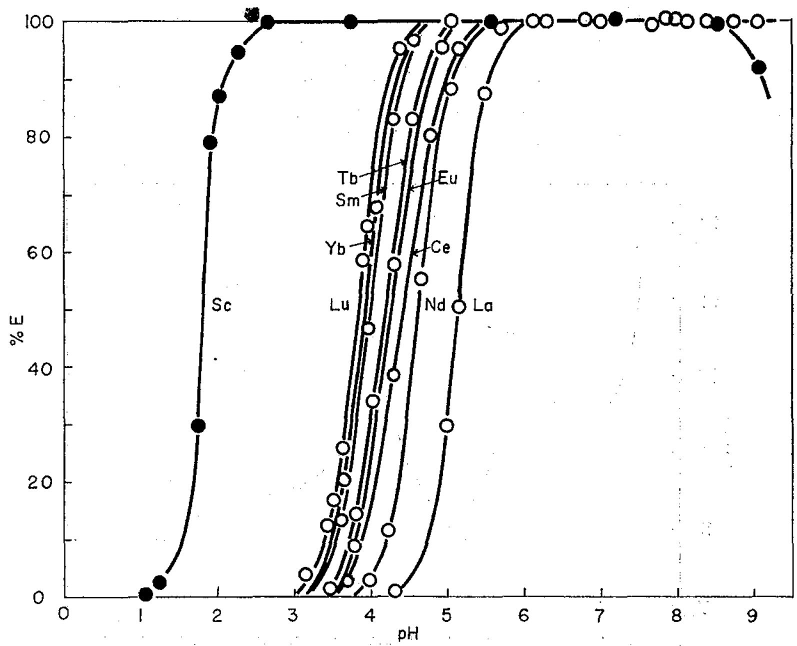

Fig. 2. The effect of pH on the extraction of trace amounts of Sc(III), La(III), Ce(III), Nd(III), Sm(III), Eu(III), Tb(III), Yb(III), and Lu(III)-0.05 M benzoyltrifluoroacetone-benzene system.

organic reagent may be expressed as:

$$-\Delta G = \mathrm{RT} \log K = \mathrm{const.} \times \mathrm{pH}_{1/2} = \mathrm{const.} \times n/r,$$ [5]

where n is the charge and r is the crystal radius of the metal ion. In Fig. 3, the extraction constants, K, of the extractable chelates are plotted as a function of the ionic potentials.

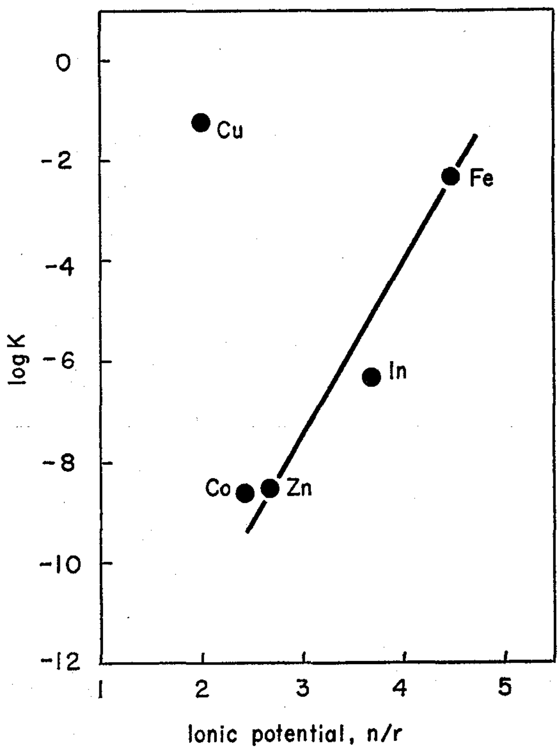

Fig. 3. The apparent extraction constant, logK, in the metal-benzoyltrifluoroacetone–benzene systems as a function of the ionic potential.

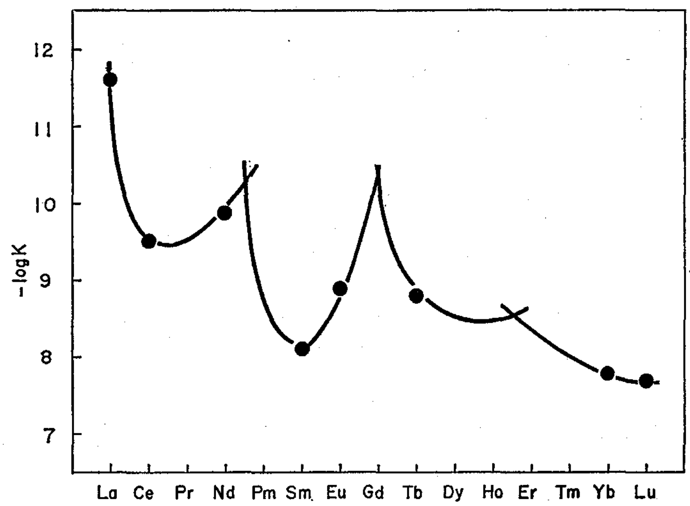

Fig. 4. The variation of the extraction constants of rare earth benzoyltrifluoroacetonates with atomic number of rare earth elements.

The results show that the apparent extraction constants for the benzoyltrifluoroacetonate chelates tend to increase with an increase in the ionic potential of the metals. Similar results have been obtained in acetylacetone[6] and benzoylacetone[7] chelate system; that is, in all the $pH_{1/2}$ decreases in the ionic radii or the ionic potential. The high stability of copper chelates is attributed to its high ionization potential. However, it should be noticed that the apparent extraction constants for the monothiothenoyltrifluoroacetone chelates tend to decrease with an increase in the ionic potential of the metals,[8] because the oxygen–sulfur-donating ligand has a marked tendency to form covalent bond due to $d\pi$–$d\pi$ inter-

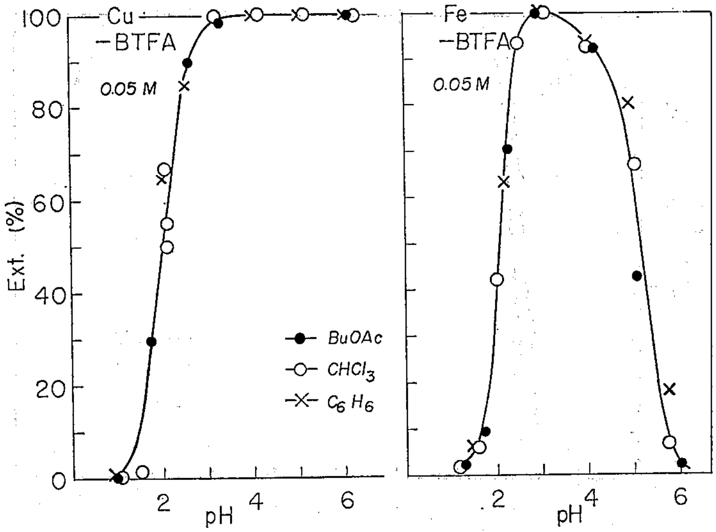

Fig. 5. Extraction of copper(II) and iron(III) with 0.05 M benzoyltrifluoroacetone in butylacetate, benzene, and chloroform as a function of pH.

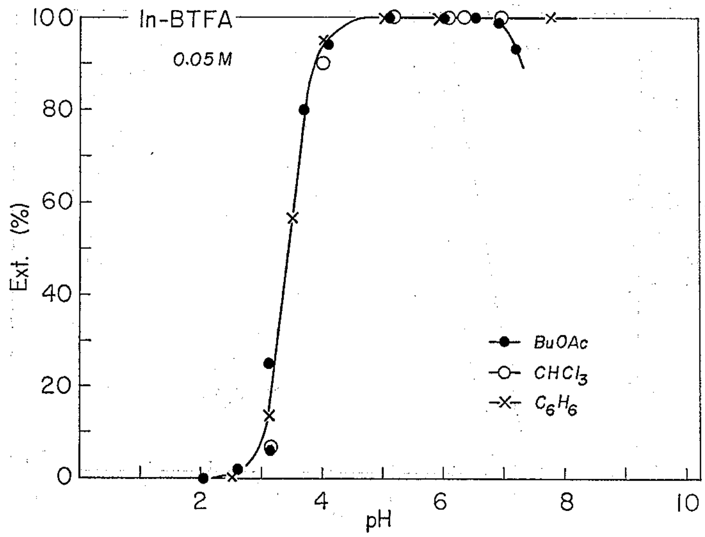

Fig. 6. Extraction of indium(III) with 0.05 M benzoyltrifluoroacetone in butylacetate, benzene, and chloroform as a function of pH.

actions. The stability of the complex of the first-transition elements follows Irving and Williams' order of stability,[9] that is, Ni<Cu>Zn, regardless of the nature of the coordination ligand. In the solvent extractions of the benzoyltrifluoroacetone chelates of these metals, a similar sequence is observed. In rare earth elements-benzoyltrifluoroacetone-benzene extraction system, the value of $pH_{1/2}$ rises as the ionic radius of the central rare earth metal increases,[2] while the variation of the extraction constants of rare earth chelates, $-\log K$, with atomic number of rare earth elements, Z, showed interesting tetrad effects as shown in Fig. 4. The extraction curves for copper-, iron-, indium-, scandium-, uranium-, neo-

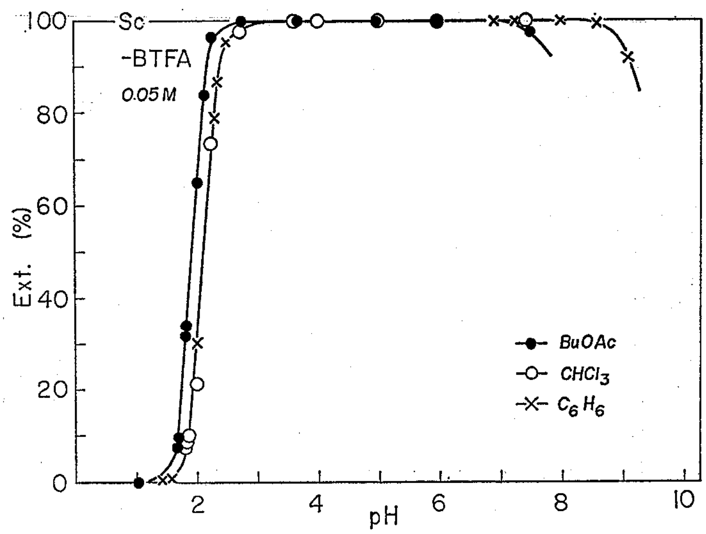

Fig. 7. Extraction of scandium(III) with 0.05 M benzoyltrifluoroacetone in butylacetate benzene, and chloroform as a function of pH.

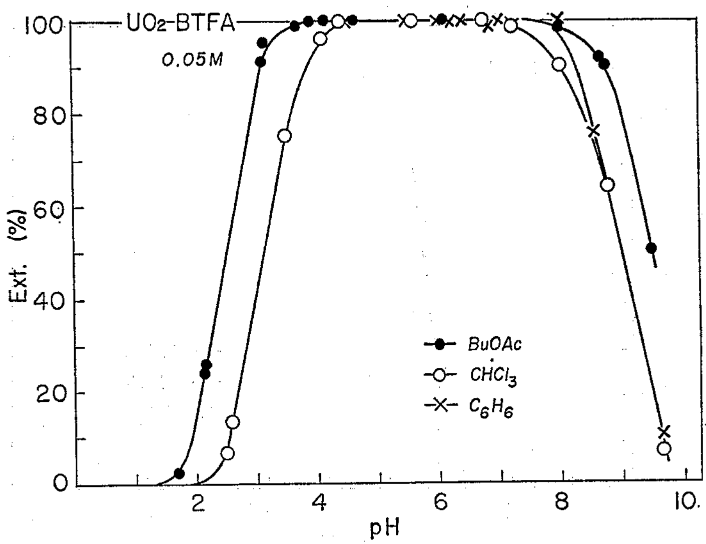

Fig. 8. Extraction of uranium(VI) with 0.05 M benzoyltrifluoroacetone in butylacetate, benzene, and chloroform as a function of pH.

dymium-, europium- and lutetium-benzoyltrifluoroacetonates with butylacetate, chloro form, and benzene are shown in Figs. 5–11. From the figures, it is clear that the extraction of rare earth and uranyl benzoyltrifluoroacetonates proceeds better with butylacetate than with chloroform or benzene. This phenomenon, the synergistic enhancement of metal chelate extraction, may be caused by the formation of rare earth and uranyl chelate adducts with butylacetate having active oxygen atom, as have already been pointed out in the previous paper.[2] In conclusion, quantitative extraction of metals using benzoyltrifluoroacetone could be achieved at a lower pH region from the lower pK_D value like 9.20 in 75%

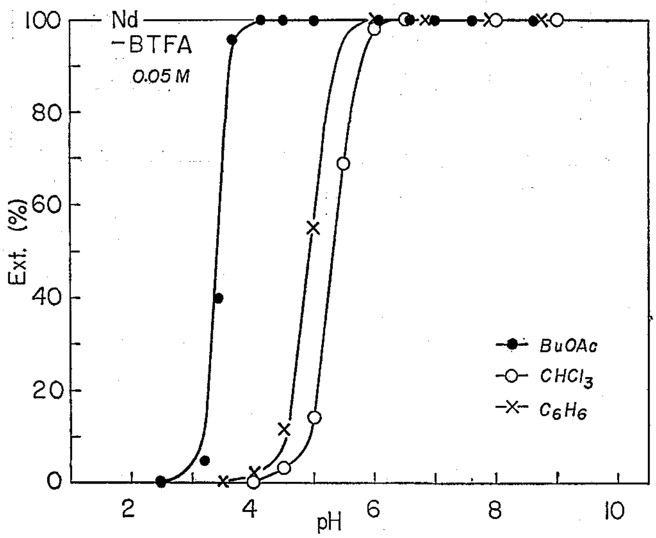

Fig. 9. Extraction of neodymium(III) with 0.05 M benzoyltrifluoroacetone in butylacetate, benzene, and chloroform as a function of pH.

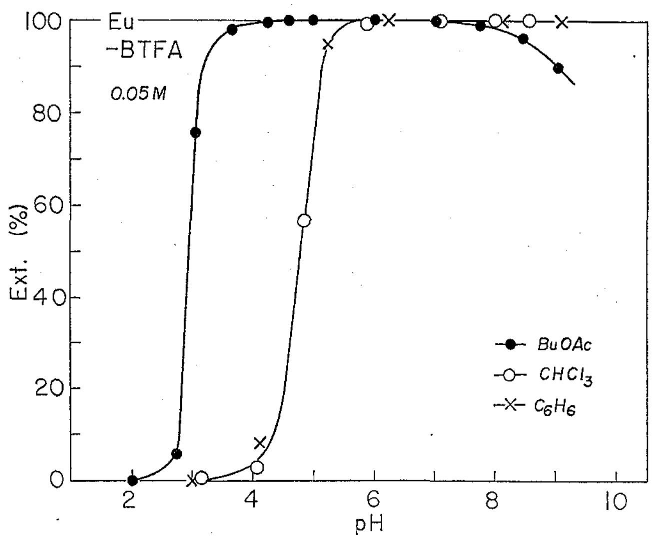

Fig. 10. Extraction of europium(III) with 0.05 M benzoyltrifluoroacetone in butylacetate, benzene, and chloroform as a function of pH.

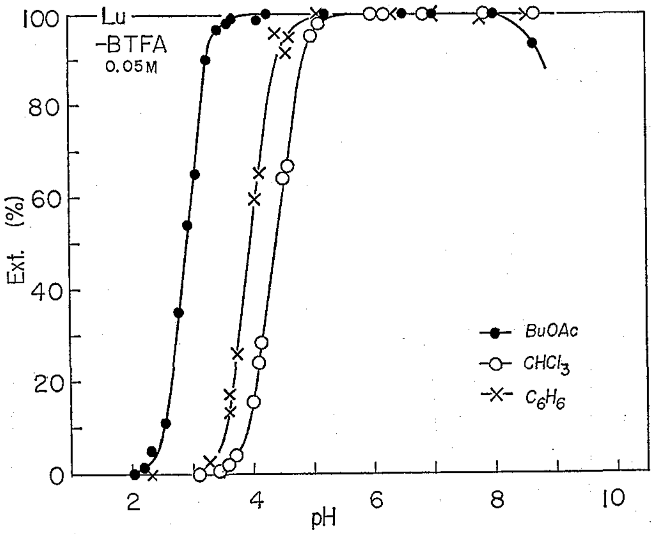

Fig. 11. Extraction of lutetium(III) with 0.05 M benzoyltrifluoroacetone in butylacetate, benzene, and chloroform as a function of pH.

(v/v) dioxane[10] and 6.03 in water.[11] This may be due to the electron-withdrawing fluoromethyl group. Moreover high extractability was found to be achieved from its low solubility in water, and the extraction may be facilitated by the shielding effect of the phenyl group against hydration to the central metal. This phenomenon may be attributed to the high distribution coefficient between water and benzene like log Pr=2.61.[11]

REFERENCES

(1) A. K. De, S. M. Khopkar, and R. A. Chalmers, "Solvent Extraction of Metals." Van Nostrand Reinhold Company, Ltd, London, 1970.
(2) T. Shigematsu and T. Honjo, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 613 (1969).
(3) T. Shigematsu, M. Tabushi, and M. Matsui, *Bull. Chem. Soc. Japan*, **37**, 1333 (1964).
(4) M. Ishibashi, T. Shigematsu, and Y. Nishikawa, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **77**, 1479 (1956).
(5) D. Dyrssen, *Svensk Kem. Tidskr.*, **68**, 212 (1956).
(6) T. Shigematsu and M. Tabushi, *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 35 (1961).
(7) J. Stary and E. Hladky, *Anal. Chim. Acta*, **28**, 227 (1963).
(8) T. Honjo, S. Yashima, and T. Kiba, *Bull. Chem. Soc. Japan*, **46**, 3772 (1973).
(9) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, **1953**, 3192.
(10) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Amer. Chem. Soc.*, **75**, 457 (1953).
(11) T. Sekine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nucl. Chem.*, **35**, 3968 (1973).