Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Extraction of Platinum(IV) with Trioctylamine and its Application to Liquid Membrane Transport

Jianshun Fu[a]; Shigeto Nakamura[a]; Kenichi Akiba[a]
[a] INSTITUTE FOR ADVANCED MATERIALS PROCESSING TOHOKU UNIVERSITY, SENDAI, JAPAN

To cite this Article Fu, Jianshun , Nakamura, Shigeto and Akiba, Kenichi(1995) 'Extraction of Platinum(IV) with Trioctylamine and its Application to Liquid Membrane Transport', Separation Science and Technology, 30: 4, 609 — 619
To link to this Article: DOI: 10.1080/01496399508225612
URL: http://dx.doi.org/10.1080/01496399508225612

SEPARATION SCIENCE AND TECHNOLOGY, 30(4), pp. 609–619, 1995

Extraction of Platinum(IV) with Trioctylamine and Its Application to Liquid Membrane Transport

JIANSHUN FU, SHIGETO NAKAMURA, and KENICHI AKIBA
INSTITUTE FOR ADVANCED MATERIALS PROCESSING
TOHOKU UNIVERSITY
KATAHIRA-2, AOBA-KU, SENDAI 980, JAPAN

ABSTRACT

The extraction and stripping behavior of platinum(IV) between trioctylamine (TOA) in kerosene and different aqueous media has been investigated. Perchlorate anion was found to be most effective for the stripping of platinum under acidic and neutral conditions. The transport of platinum was performed through a supported liquid membrane (SLM) impregnated with TOA as a mobile carrier. Platinum was almost quantitatively transported from the hydrochloric acid solution to the stripping solutions containing perchlorate anion against its large concentration gradient without accumulation in the liquid membrane layer. The transport behavior of platinum was greatly improved by the addition of 1-octanol in SLM, and the permeation rate was mainly controlled by diffusion in the aqueous boundary layer.

INTRODUCTION

A supported liquid membrane consisting of a combination of extraction and stripping processes of desired species appears particularly promising for many kinds of separation processes. This technique is potentially useful provided that suitable mobile carriers and stripping reagents are available.

Solvent extraction of platinum group metals (PGMs) has been extensively studied by adopting varieties of extractants, including many chelating reagents having a high selectivity for some individual elements of PGMs (1). However, applications of these extraction systems to membrane transport of PGMs have been limited to a few cases due to their slow extraction kinetics and difficulties in stripping (2, 3). In addition, a tendency to precipitate as complex species of PGMs in some systems may cause practical problems in the quantitative transport of metals (4, 5). Certain amines have strong extractability and good kinetic behavior to most PGMs, but their poor stripping problems are not still solved (3). The transport of metal species across a liquid membrane depends not only on the equilibrium distribution ratios but on the kinetics in extraction and stripping processes.

The present paper is concerned with the solvent extraction of Pt(IV) with trioctylamine; in particular, the stripping behavior with various stripping solutions and its application to a membrane transport system.

EXPERIMENTAL

Materials

Trioctylamine (TOA, Wako Pure Chemical Ind.) of more than 97% purity was diluted with kerosene. A platinum solution was prepared by diluting a standard solution containing 1000 ppm platinum(IV) in 1 M (M = $mol{\cdot}dm^{-3}$) HCl. Other chemicals employed were of guaranteed reagent grade. A microporous polytetrafluoroethylene membrane (Fluoropore FP-045, Sumitomo Electric Ind.), 80 μm thick, with 74% porosity, and of 0.45 μm pore size, was used as a solid support.

Extraction and Stripping of Platinum(IV)

An aqueous solution and an equal volume of an organic solution were shaken at 25°C for 5 minutes unless otherwise noted. After phase separation by centrifugation, the concentration of Pt(IV) in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The concentration of Pt(IV) in the organic phase was evaluated from the difference between the concentrations of Pt(IV) in the aqueous phase before and after extraction.

Transport of Platinum(IV)

An experimental apparatus for measuring the permeation rates of Pt(IV) was composed of inner and outer polypropylene vessels (6). A microporous support (26 cm^3) was attached to the bottom of inner vessel and impregnated with a kerosene solution of TOA. A feed solution of 0.5 M HCl (100 cm^3) initially containing 2.56×10^{-4} M Pt(IV) was placed in the outer vessel, and usually an equal volume of the product solution was placed in the inner vessel. The apparatus was shaken at 120 strokes per minute (spm) in a water bath at 25°C. Portions of the feed and product solutions were periodically sampled, and the concentrations of Pt(IV) were determined by ICP-AES.

RESULTS AND DISCUSSION

Extraction of Platinum(IV) with TOA

Amines with long chains have high extraction ability for PGMs; for example, the extraction of Pt(IV) with TOA (R_3N) from hydrochloric acid solution is written as (7)

$$R_3N_{org} + HCl_{aq} \rightleftharpoons R_3NHCl_{org} \quad (1)$$

$$2R_3NHCl_{org} + PtCl_{6,aq}^{2-} \rightleftharpoons (R_3NH)_2PtCl_{6,org} + 2Cl_{aq}^{-} \quad (2)$$

This extraction reaction proceeds fast and lies greatly to the right (8). As Fig. 1 shows, Pt(IV) was quantitatively extracted with 0.1 M TOA in kerosene below 2 M HCl, and 86% of Pt(IV) was extracted even at 9 M HCl. The high extractability suggests that stripping with concentrated HCl is not a practical scheme for the liquid membrane transport of Pt(IV), and that other suitable reagents are required for sufficient stripping.

Stripping of Pt(IV)

Optimum stripping conditions are essential to apply the above extraction system to a membrane transport system. Several prospective reagents were tested as stripping solutions for Pt(IV) from the loaded TOA solution. Stripping of Pt(IV) was performed with acids and salts by breaking the

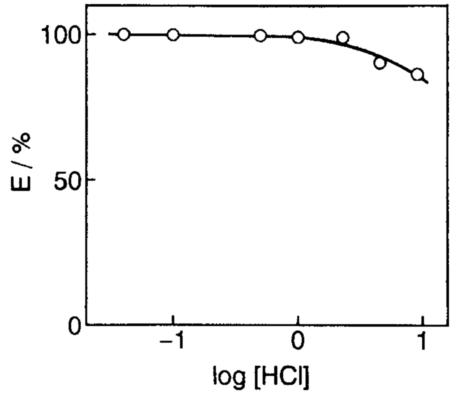

FIG. 1 Effect of HCl concentration on the extraction of platinum with 0.1 M TOA in kerosene.

ion pair and some strong coordinating ligands like thiourea (tu). As seen in Fig. 2, Pt(IV) was stripped in a short time except for the case of tu. The slow stripping rate with tu is due to low substitution kinetics for Pt(IV) having the d^6 electron configuration (9). The stripping ability for Pt(IV) decreased in the order: $HClO_4$, $NaClO_4$ > dimethylamine, NH_3 > HNO_3 > NaSCN > tu/HCl. Perchloric acid and its salt were found to be most effective for stripping, and the reaction can be described by

$$(R_3NH)_2PtCl_{6,org} + 2ClO^-_{4,aq} \rightleftharpoons 2R_3NHClO_{4,org} + PtCl^{2-}_{6,aq} \quad (3)$$

In acid solutions, TOA extracts an acid (HX) to form the alkylammonium salt

$$R_3N_{org} + HX_{aq} \rightleftharpoons R_3NHX_{org} \quad (4)$$

The affinity of anions for R_3NH^+ decreases in the order (10) ClO_4^- > NO_3^- > Cl^- > HSO_4^-. Among these anions, ClO_4^-, which has the highest affinity for R_3NH^+, appears to be the best stripping anion. As illustrated in Fig. 3, the D value decreased with increasing $HClO_4$ concentration to a low enough value to readily strip Pt(IV). When $HClO_4$ is employed as the product solution in the transport process, the reaction of Eq. (3) proceeds to the right, forming R_3NHClO_4 in the product side of the SLM. Hence, because of the difference in the distribution ratio between the feed and product sides, Pt(IV) can be transported across the membrane.

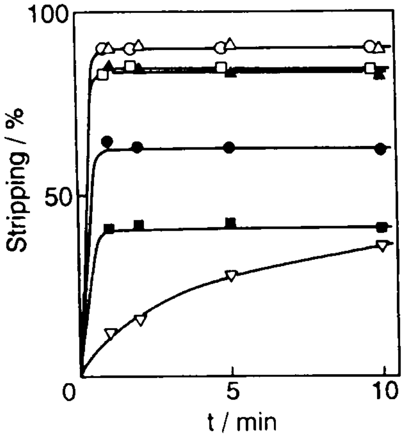

FIG. 2 Stripping of platinum from the loaded TOA solution. Organic phase: 0.1 M TOA in kerosene; aqueous phase: (○) 2 M $HClO_4$, (□) 10% dimethylamine, (■) 0.5 M NaSCN, (▽) 0.5 M tu/0.5 M HCl, (●) 2 M HNO_3, (△) 2 M $NaClO_4$, (▲) 8.3% NH_3.

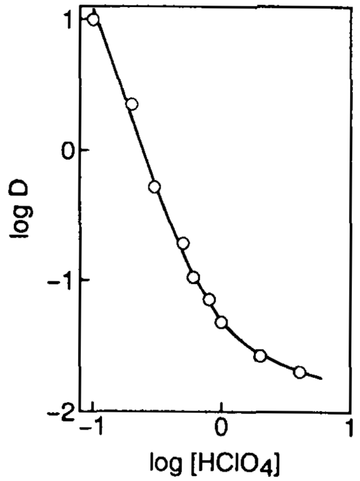

FIG. 3 Effect of $HClO_4$ concentration on the distribution ratio of platinum with 0.1 M TOA in kerosene.

Application to the Transport of Platinum(IV) through SLM

Based on its favorable extraction and stripping behavior, this TOA extraction system was applied to the liquid membrane transport of Pt(IV). The transport of Pt(IV) through SLM containing 0.5 M TOA was carried out from 0.5 M HCl solution to 1 M $HClO_4$ solution. Figure 4 shows the time-dependent fractions of Pt(IV) both in the feed and product solutions.

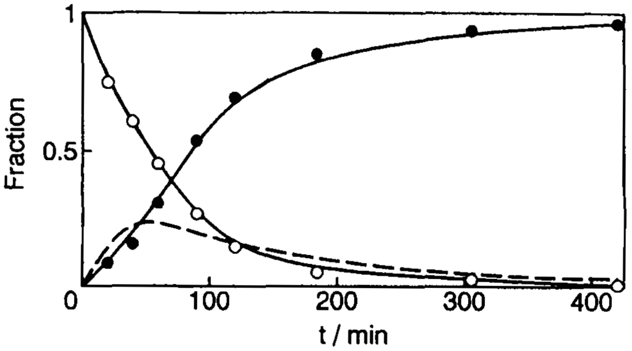

FIG. 4 Transport of platinum through SLM containing 0.5 M TOA in kerosene. Feed: 0.5 M HCl; product: 1 M $HClO_4$. (○) Feed; (●) product. The broken line corresponds to the fraction remaining in the membrane phase.

The Pt(IV) fraction in the feed solution smoothly decreased with shaking time, and that in the product solution increased at a slower rate. Then a considerable time lag was observed; for example, the time of one-half transport in the product side was delayed about 30 minutes compared with the decreasing time in the feed side. The Pt(IV) fraction remaining in the membrane phase was estimated from the difference in the fractions experimentally determined in the feed and product sides. Variation in this estimated fraction is depicted as a function of time by the broken line in Fig. 4. This remaining fraction might be due to insufficient stripping.

In liquid–liquid extraction, the third phase containing Pt(IV) was found on the boundary of organic and aqueous phases, and a similar third phase was also observed on SLM in the product side, in which the Pt(IV) species was hardly stripped to the product solution. Further, in these transport experiments, a portion of the liquid membrane gradually leached out into the aqueous solutions, and the SLM must be mended by impregnating the organic phase about every 2 hours.

As for other stripping reagents, only a small portion (<30% at 5 hours) of Pt(IV) was transported by 10% dimethylamine, with a large portion of Pt(IV) remaining in the membrane phase. Dimethylamine itself was back-transferred from the product to the feed solution. In the case of 0.5 M NaSCN, Pt(IV) was transported to a considerable extent. However, Pt–SCN complexes built up as orange-yellow deposits in the feed side of the SLM. Among the reagents tested, perchloric acid and perchlorate salt were found to be most suitable for stripping Pt(IV).

Addition of 1-Octanol in SLM

In order to accomplish sufficient striping to reduce the Pt(IV) fraction in the membrane layer, the liquid membrane was modified by the addition of a long-chain alcohol. Figure 5 illustrates the effect of 1-octanol contents on the distribution ratios of Pt(IV) between 0.5 M TOA in kerosene and 0.5 M $HClO_4$. The distribution ratio of Pt(IV) decreased with increasing 1-octanol content. This appears to be due to a decrease in free TOA concentration by the reaction between TOA and 1-octanol (11). This will serve to promote the stripping of Pt(IV) from the TOA SLM.

Transport of Pt(IV) through an SLM containing 1-octanol is shown in Fig. 6. Decreasing fractions in the feed side were only slightly affected by the 1-octanol content, but increasing fractions in the product side were greatly enhanced with increasing 1-octanol content. With a 1-octanol content of 10–20%, the Pt(IV) fractions in both sides were approximately equal, indicating that Pt(IV) accumulation in the SLM was practically

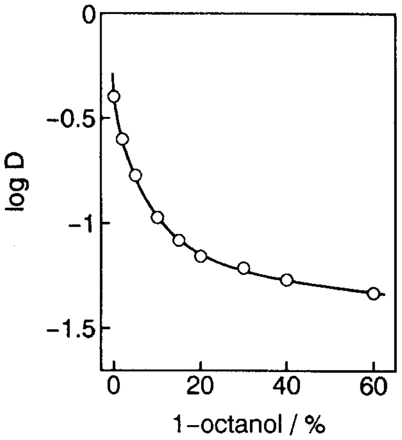

FIG. 5 Effect of 1-octanol contents on the distribution ratio of platinum. Organic phase: 0.5 M TOA in kerosene; aqueous phase: 0.5 M $HClO_4$.

negligible. Thus permeation of Pt(IV) through the TOA liquid membrane was promoted by the addition of 1-octanol.

Long-chain alcohols sometimes play an important role in a transport process (12). As for the TOA system, besides those advantages described above, the third phase containing Pt(IV) was readily overcome by the addition of 1-octanol. Furthermore, the SLM was stabilized to be effective for about 5 hours without loss of the carrier in the presence of 20% 1-octanol.

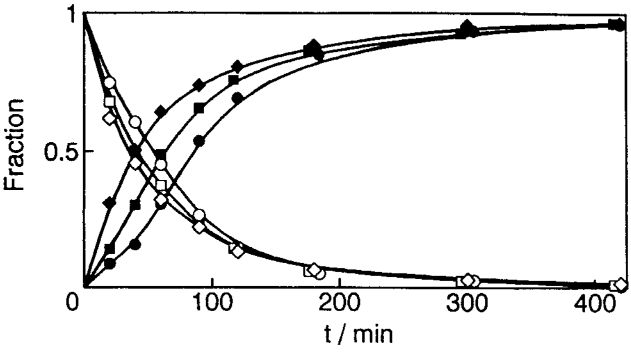

FIG. 6 Effect of 1-octanol contents on the transport of platinum. Feed: 0.5 M HCl; product: 1 M $HClO_4$; SLM: 0.5 M TOA and (○, ●) 0%, (□, ■) 5%, (◇, ◆) 20% 1-octanol in kerosene. Open symbols: feed; filled symbols: product.

Effect of TOA Concentration

The quantitative transport of Pt(IV) was accomplished through an SLM impregnated with 0.1–0.8 M of TOA in the presence of 20% 1-octanol. The apparent rate constant, $k_{f,obs}$, for the transport of Pt(IV) is evaluated from the following equation:

$$\ln([Pt]_{f,t}/[Pt]_{f,0}) = -k_{f,obs}t \tag{5}$$

The $k_{f,obs}$ value increased slightly with TOA concentration, as shown in Fig. 7.

Effect of $HClO_4$ Concentration

Figure 8 shows the transport of Pt(IV) into different concentrations of $HClO_4$. The experimental results on transport are summarized in Table 1; the value of $k_{f,obs}$ almost remained unaltered below 1.0 M $HClO_4$, and further increasing the $HClO_4$ concentration led a slight drop in $k_{f,obs}$. This is difficult to explain from liquid–liquid extraction data. One reason may be that a small amount of ClO_4^- in the product solution permeated through the SLM to the feed side and lowered the extractability of Pt(IV). Although insufficient stripping occurred only at low concentrations (such as 0.1 M), Pt(IV) was almost quantitatively transported into the $HClO_4$ solution above 0.5 M after 9 hours.

Concentration Factor

The product volume was set much smaller than the volume of the feed solution to concentrate Pt(IV) into the product solution. The values of

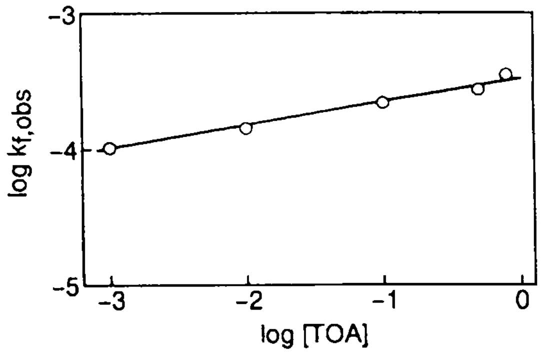

FIG. 7 Effect of TOA concentration on the apparent rate constant. SLM: TOA–20% 1-octanol in kerosene; feed: 0.5 M HCl; product: 1 M $HClO_4$.

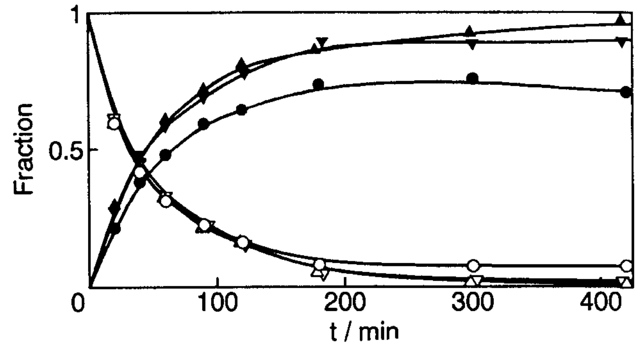

FIG. 8 Effect of $HClO_4$ concentration on the transport of platinum. SLM: 0.5 M TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: (○, ●) 0.1 M, (▽, ▼) 0.3 M, (△, ▲) 1.0 M $HClO_4$. Open symbols: feed; filled symbols: product.

the concentration gradient $[Pt]_p/[Pt]_f$ and the concentration factor $[Pt]_p/[Pt]_{f,0}$ after 9 hours are listed in Table 1. Pt(IV) in HCl solution was transported into the $HClO_4$ solution against its large concentration gradient. The concentration factors obtained were close to the corresponding ratio of the feed volume (V_f) and the product volume (V_p). Even when the concentration factor was as high as nearly 20, more than 97% of the initial Pt(IV) was recovered in the product solution. Thus, the SLM with TOA carrier can be successfully utilized in the separation and concentration of Pt(IV) from dilute solutions.

TABLE 1
Transport and Concentration of Platinum(IV)[a]

$HClO_4$ (M)	V_p (cm^3)	V_f/V_p	$k_{f,obs}$ (s^{-1})	$[Pt]_p/[Pt]_f$ at 9 hours	$[Pt]_p/[Pt]_{f,0}$ at 9 hours	Recovery at 9 hours (%)
0.1	100	1	3.13×10^{-4}	10	0.674	67.4
0.3	100	1	3.10×10^{-4}	34	0.916	91.6
0.5	100	1	3.12×10^{-4}	62	0.970	97.0
1.0	100	1	3.17×10^{-4}	96	0.973	97.3
3.0	100	1	2.50×10^{-4}	100	0.981	98.1
3.0	25	4	2.62×10^{-4}	650	3.92	98.8
3.0	10	10	2.60×10^{-4}	1324	9.71	97.3
3.0	5	20	2.55×10^{-4}	3275	19.3	97.2

[a] Feed: 0.5 M HCl, 100 cm^3. SLM: 0.5 M TOA and 20% 1-octanol in kerosene.

Effect of Pt(IV) Concentration

The influence of the initial Pt(IV) concentration in the feed side on transport across an SLM containing 0.5 M TOA–20% 1-octanol is shown in Fig. 9. The initial Pt(IV) flux through an SLM, J (mol·cm^{-2}·s^{-1}), is given by

$$J = \left(\frac{d[\mathrm{Pt}]_{\mathrm{f},t}}{dt}\right)_{t=0} \frac{V_{\mathrm{f}}}{S} \tag{6}$$

where S refers the geometric area of the SLM.

At low concentration regions below 10^{-3} M $[\mathrm{Pt}]_{\mathrm{f},0}$, the flux varied in proportion to the initial Pt(IV) concentration, beyond which it reached a constant value. Further increasing the Pt(IV) concentration produced an orange-yellow deposit on the SLM in the feed side.

Effect of Shaking Speed

Figure 10 illustrates the effect of shaking speed on the transport rate of Pt(IV). The $k_{\mathrm{f,obs}}$ value increased with shaking speed up to 130 spm, and then decline with any further increase in shaking speed because TOA was partially leached out from the SLM at too high a speed. Increasing $k_{\mathrm{f,obs}}$ with increasing shaking speed may be attributable to a decrease in the thickness of the boundary layer between the feed solution and the SLM (13).

In conclusion, TOA can successfully serve as a carrier to transport Pt(IV) from a dilute HCl solution to a $HClO_4$ solution. Pt(IV) can be

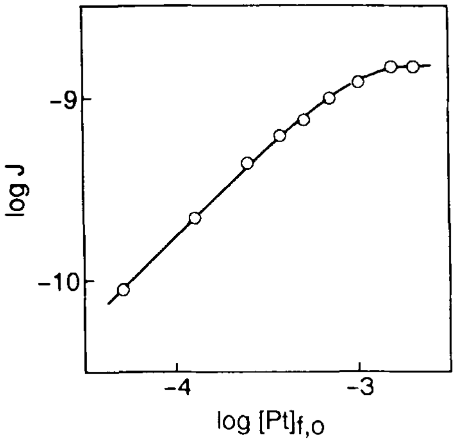

FIG. 9 Effect of initial concentration of platinum in the feed solution on the flux. SLM: 0.5 M TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: 1 M $HClO_4$.

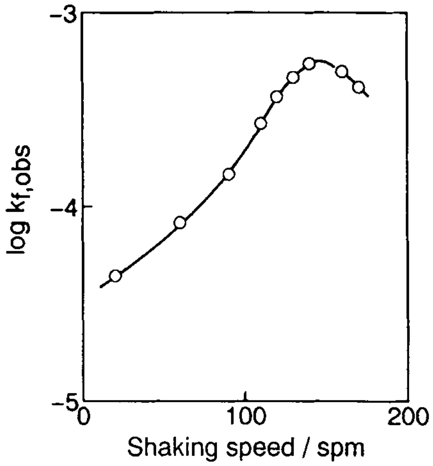

FIG. 10 Effect of shaking speed on apparent rate constant. SLM: 0.5 M TOA and 20% 1-octanol in kerosene; feed: 0.5 M HCl; product: 1 M $HClO_4$.

almost quantitatively transported across an SLM containing 0.5 M TOA and 20% 1-octanol to the product solution at an excellent rate ($k_{f,obs} > 2.50 \times 10^{-4}$). The total transport of Pt(IV) may be primarily controlled by the diffusion process in the aqueous boundary layer.

REFERENCES

1. L. M. Gindin, *Ion Exchange and Solvent Extraction*, Dekker, New York, 1981, p. 311.
2. S. J. Al-Bazi and H. Freiser, *Solv. Extr. Ion Exch.*, *4*, 1121 (1986).
3. G. Pouskouleli, *Separation Processes in Hydrometallurgy*, Ellis Horwood, Chichester, 1987, p. 174.
4. E. Antico et al., *Solvent Extraction 1990*, Elsevier, Amsterdam, 1992, p. 1505.
5. A. Warshawsky, *Sep. Purif. Methods*, *9*, 209 (1980).
6. K. Akiba and T. Kanno, *Sep. Sci. Technol.*, *18*, 831 (1983).
7. S. C. Dara, *Precious Metals: Mining, Extraction and Processing*, Metallurgical Society, AIME, Warrendale, New Jersey, 1984, p. 199.
8. M. Cox, *Developments in Solvent Extraction*, Ellis Horwood Press, Chichester, 1988, p. 177.
9. M. J. Cleare, P. Charlesworth, and D. J. Bryson, *J. Chem. Tech. Biotechnol.*, *29*, 210 (1979).
10. C. F. Coleman et al., *Ind. Eng. Chem.*, *50*, 1756 (1958).
11. E. Högfeldt, *Developments in Solvent Extraction*, Ellis Horwood Press, Chichester, 1988, p. 36.
12. S. Nakamura and K. Akiba, *Sep. Sci. Technol.*, *24*, 673 (1989).
13. S. Nakamura, S. Ohashi, and K. Akiba, *Ibid.*, *27*, 741 (1992).

Received by editor February 24, 1994